

# Thermoreversible and salt-sensitive turbidity of methylcellulose in aqueous solution

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## Abstract

The turbidity of methylcellulose (MC) aqueous solutions without or with salt was investigated by optical transmittance. The optical transmittance was found to decrease with heating, while it recovered upon cooling. This phenomenon reflected the micro-phase transition from an unassociated state to a hydrophobically associated state in the solution when the system underwent the sol–gel transition. The derivative of absorbance ( $dA/dT$ ) was used to determine the clouding point during gelation and the melting point during degelation. A salt-out salt (NaCl), a salt-in salt (NaI) and a salt mixture (NaCl+NaI) were, respectively, added into a MC solution to further investigate effects of salts on the gelation behavior. The critical transition temperatures obtained from rheological and micro thermal measurements were found to be consistent with the clouding points obtained by turbidity measurements. In the MC solutions with the salt mixtures, the critical temperatures followed a linear rule of mixing, indicating that the effects of salts on the sol–gel transition of MC are completely independent. © 2005 Elsevier Ltd. All rights reserved.

*Keywords:* Sol–gel transition; Methylcellulose; Salt

## 1. Introduction

Methylcellulose (MC), a water soluble derivative of cellulose, can form thermoreversible hydrogels in water upon heating and subsequently dissolve upon cooling [1–3]. This is mainly due to the hydrophobic association that becomes pronounced at elevated temperatures at which the hydrogen bonding between MC chains and water is destroyed [4–12]. Besides temperature, the gelation of MC is well known to be sensitive to solvent [13], pH [14], electrical or magnetic field [15] and coexisting solutes including ions [16,17].

According to the ‘Hofmeister series’ [18], an order of ions ranked in terms of how strongly they affect hydrophobicity of a solute, ions may either stabilize or weaken the structure of water due to their different interactions with water molecules. Anion in a salt, believed to deliver stronger effect than cation [9,13,19–21], is the deciding factor for the salt effect. A typical Hofmeister

order for anions was reported as  $\text{SO}_4^{2-} > \text{F}^- > \text{Cl}^- > \text{Br}^- > \text{NO}_3^- > \text{ClO}_4^- > \text{I}^- > \text{SCN}^-$ . Ions on the left can be strongly hydrated, exhibiting strong interactions with water molecules. As a result, they tend to cause ‘salt-out’ or to enhance hydrophobicity of a solute in water. In contrast, ions on the right can be weakly hydrated, tending to cause ‘salt-in’, which increases the solubility of a non-polar solute. In this study,  $\text{Cl}^-$  and  $\text{I}^-$  are chosen as the representatives of salt-out and salt-in salts, respectively. In the previous studies [11,12], it is proved that heating of a MC aqueous solution is endothermic, in which the total heat is mainly attributed to the destruction of hydrogen bonds formed between MC chains and water molecules.

Over the years, different methods have been used to characterize the sol–gel transition. The most common and convenient technique is rheology, where the dynamic viscoelastic measurements for a given sample are conducted during the formation of a three-dimensional gel network structure. A sharp increase in storage modulus ( $G'$ ) to result in  $G' > G''$  ( $G''$  is the loss modulus) is generally an indication of the sol–gel transition. The plateau value of  $G'$  after the sol–gel transition is the strength of the mature gel [12,22]. Another important method used in gelation study is micro differential scanning calorimetry (micro DSC), which detects small amount of heat absorbed or

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released by the sample during a thermal process. Determination of turbidity over the sol–gel transition is another effective technique for gel study. However, this method is valid only for optically turbid gels. If the turbidity of a given gelling system increases as the system undergoes the sol–gel transition, it can be used as an indication of the microphase transition from random coils to aggregates or clusters [23–26]. The clouding behavior is considered to relate with the spatial variation of the aggregates, which results in strong scattering of light and drastic reduction in optical transmission [27]. Therefore, optical transmittance measurement can be used to characterize the development of aggregates in a gelling system and estimate the formation of a network structure.

In this work, the turbidity of MC aqueous solutions has been measured as a function of temperature and the effects of individual salts and a salt mixture on the sol–gel transition have been studied. The clouding and melting properties of MC solutions have been compared with the thermal and rheological ones to verify the gelation mechanisms and identify the relationship between them.

## 2. Experimental

### 2.1. Materials and sample preparation

A cellulose derivative, methylcellulose with a trade name of SM 4000, was obtained from Shinetsu Chemical Co. Ltd, Japan. The polymer had an average degree of substitution (DS) of 1.8 and an average molecular weight of 310,000 determined by light scattering. The viscosity was 4.54 Pa s at 20 °C for a 2 wt% aqueous solution. The material was used as received without further purification. Prior to use, it was vacuum-dried at 55 °C for 24 h and kept in a desiccator at room temperature. The salts, NaCl and NaI, were purchased from Sino Chemical Co. (Pte) Ltd, Singapore, and used as received.

A pure MC aqueous solution of 0.03 mM (about 0.93 wt%), was first prepared by dispersing the weighed MC powder into deionized water at 70 °C and kept in a refrigerator for stabilization. A homogeneous and transparent solution of MC was obtained. The weighed salt or salt mixture was then added into the MC solution to obtain all the MC-salt solutions. All the sample solutions were prepared with deionized water from a Millipore water purifier. A low temperature (below 10 °C) was used to keep the MC solutions.

### 2.2. Turbidity measurement

An ultraviolet–visible spectroscopy system (Agilent 8453, UV–vis, HP Co.) equipped with a temperature controller was employed for the turbidity measurements. The sample was placed in the cell with a dimension of  $1 \times 1 \times 5 \text{ cm}^3$ . Deionized water was used as the reference. The

cell was covered with a plastic cap to prevent evaporation. In addition to the temperature sensor, a thermocouple was placed in the sample cell for temperature measurement. The absorbance was measured at a wavelength of 500 nm through a thermal cycle in which the sample was first heated from 20 to above 80 °C and subsequently cooled back to 20 °C at a scanning rate of 1 °C/min. The absorbance was then converted to transmittance according to Beer's Law [28].

### 2.3. Rheological and microthermal measurements

The rheological tests were conducted on a fluid rheometer (ARES 100FRTN1, Rheometric Scientific) with a parallel plate of 25 mm diameter. The storage modulus ( $G'$ ) and loss modulus ( $G''$ ) were measured as a function of temperature at an angular frequency of 1 rad/s within a linear range of viscoelasticity. A micro differential scanning calorimeter (VP-DSC Microcalorimeter, Inc.) was used to determine the thermal properties of the salted MC solutions during a thermal cycle from 10 to 80 °C. After each cycle was completed, the sample and reference cells were thoroughly cleaned with a water baseline session to ensure a non-contamination condition before the next test. For consistency, all the rheological and thermal measurements were carried out at a fixed heating and cooling rate (if applicable) of 1 °C/min, which was the same as that used in the turbidity measurements.

## 3. Results and discussion

### 3.1. Turbidity during gelation

Light transmittance of a 0.03 mM salt-free MC solution at the wavelength of 500 nm is plotted in Fig. 1(a) as a function of temperature. The corresponding photos of the sample at three typical temperatures during heating, which are the transparent solution at low temperature (25 °C), the semi-gel status at the critical transition temperature (62 °C) and the complete opaque gel beyond gelation (75 °C), respectively, are presented Fig. 1(b) to illustrate the visible images of the sample at different stages of gelation.

As shown in Fig. 1, at low temperatures (<50 °C), the solution displays the high transmittance (nearly 100%), indicating that the MC solution is clear and the transmittance is independent of temperature. However, after being heated to a certain temperature near the sol–gel transition temperature, the transparent solution starts to become turbid, followed by the sharp decrease in transmittance. The sample becomes completely opaque within a narrow temperature range, and the transmittance drops to about zero after an integrated, cloudy and solidified gel is formed as seen in the photo.

The decrease in transmission is believed to be due to the formation of large clusters or aggregates and eventually a

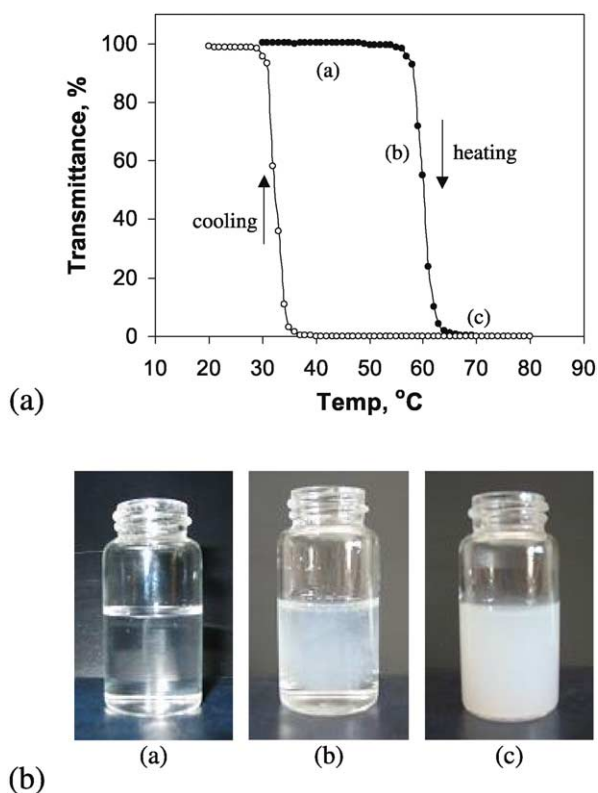


Fig. 1. (a) Optical transmittance of a 0.03 mM MC solution at a wavelength of 500 nm during heating (filled circles) and cooling (empty circles) at a scanning rate of 1 °C/min. (b) Photos representing the samples at three different stages of gelation, which are a clear solution at 25 °C, a semi-gel at 62 °C and a mature gel at 75 °C, respectively.

gel network structure during heating, which leads to the strong light scattering. It should be true that the denser a gel network formed, the lower the optical transmission is. Sloomackers et al. [29] in their studies on clouding behavior of carrageenan solutions and Nossal's work [30] 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.

MC shows a good solubility in water at low temperatures due to the hydrogen bonds between water molecules and the MC chains, and/or the cage-like structures surrounding the methyl groups [11,12]. The solution in this state is clear with a nearly 100% transmittance. Heating of the MC solution causes the destruction of the hydrogen bonds, and the exposure of hydrophobic regions of MC, leading to the formation of MC hydrophobic aggregates or the so-called hydrophobic association. This is corresponding to a morphological change from the MC random coils to the intermolecular hydrophobic association. As temperature increases, the number and the size of hydrophobic aggregates grow, resulting in a great absorbance and/or light scattering. As a result, the sharp decrease in light

transmission is observed. Another important feature in Fig. 1 is that the gelling process, which is always accompanied by a balance between the hydrophobic association and dissociation, is gradual and continuous, leading to a homogeneous formation of gel network structure. Thus, this sol–gel transition process is achieved by the so-called micro-phase separation rather than the macro-phase separation. The latter may tend to cause precipitation.

In the subsequent cooling process, 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 loop, 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 cooling and heating indicates that the thermally induced hydrophobic dissociation is not an exact reversal of the hydrophobic association occurring in the heating process.

Gelation has been extensively characterized by measuring clouding point. Jonsson et al. [24] defined the clouding point as the temperature at which the phase separation occurs for 1% polymer concentration. In a practical application of clouding point method, however, different ways may be used to obtain the clouding point. Emergayer et al. [31], for instance, defined the intersection of two straight lines drawn through the curves of absorbance at low and high temperatures, respectively, as the cloud point, or the onset temperature when the absorbance starts to increase. Zheng et al. [28] defined the 50% transmittance as the clouding point or the sol–gel transition temperature. In this study, the critical transition temperature is determined through the first derivative of absorbance because we found that this way is more rigorous than the existing ones.

In Fig. 2, the derivative of absorbance with respect to temperature ( $dA/dT$ ) is given as a function of temperature, where there exhibits one peak each for both heating and cooling periods. The peak temperatures are defined as the clouding point and the melting point during the sol–gel and the gel–sol transition, respectively. This definition is more reasonable for the MC gelling system by considering the gelation mechanism involved from the molecular origin. For example, during heating the derivative of absorbance remains low (close to zero) at the beginning, implying that the absorbance is independent of temperature in the low temperature range. The derivative rises sharply after about 55 °C, which can be explained by the increased absorbance due to the appearance of the region of hydrophobic clusters or aggregates of MC chains. The hydrophobic aggregates, both in size and in number, are growing in an accelerated path until reaching the peak point at 62.9 °C. Beyond the peak, the increase in absorbance slows down although

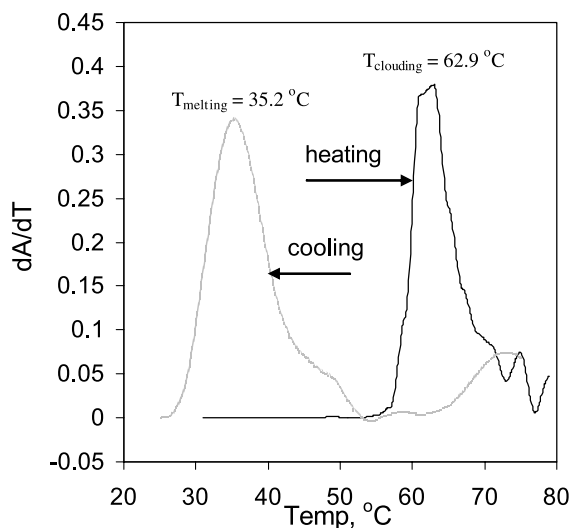


Fig. 2. First derivative of absorbance ( $dA/dT$ ) at a wavelength of 500 nm for a 0.03 mM MC solution during heating and cooling. The peak temperatures ( $62.9\text{ }^{\circ}\text{C}$  in heating and  $35.2\text{ }^{\circ}\text{C}$  in cooling) are defined as the clouding point for gelation and the melting point for degelation, respectively.

the sample continues to become more turbid, since, the derivative value maintains positive. It is obvious that the development of aggregates now levels off, and the number and the size of the aggregates are great enough to be physically cross-linked into an integrated network structure. As a result, more light is scattered until the transmittance falls to nearly zero after a mature gel is eventually formed. Therefore, the temperature at which the first derivative of absorbance reaches the peak is the critical point in the sol–gel transition, and the gel network starts to form from the temperature. In the cooling curve, the melting point is obtained as the peak temperature ( $35.2\text{ }^{\circ}\text{C}$ ) of the respective derivative curve. These two peaks and the difference between them are correlated with the thermodynamic behavior of MC in water, showing that both the gelation and degelation are kinetic processes. It is noticed that the cooling curve is smoother and broader than that of heating, which might be due to a slower degelation process than gelation.

### 3.2. Salt-induced clouding behavior of MC solutions

The following results were obtained from the MC aqueous solutions containing an individual salt (NaCl or NaI) or a salt mixture of NaCl and NaI with different compositions. The MC concentration was fixed at 0.03 mM for all the salted aqueous solutions. The effects of salt on turbidity were examined when the samples undergo gelation and degelation.

Fig. 3 shows the light transmission of the MC solutions with different NaCl contents during heating and cooling. It is obvious that all NaCl-added samples follow the similar pattern as that of the salt-free MC solution in terms of light transmittance during the thermal cycle. At low tempera-

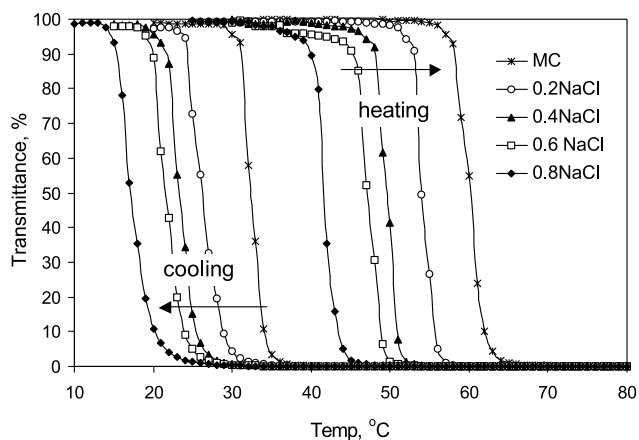


Fig. 3. Turbidity behavior of MC solutions with various concentrations of salt-out salt (NaCl) in a thermal cycle at a wavelength of 500 nm.

tures, the samples are clear with high light transmittance, corresponding to a stable sol state. Heating to an elevated temperature makes the samples become turbid, and the light transmission falls sharply within a narrow temperature range until close to zero, implying that the incident light has totally been scattered due to the formation of a gel in the system. As for cooling, the turbidity remains high until a certain critical temperature. When the gel starts to melt, the sample returns transparent with a high transmittance after cooling back to low temperatures. The similarity of all the curves indicates that the clouding and melting behaviors or the gelation and degelation mechanisms of MC, are similar. The only difference among the curves is the temperature at which the sample becomes cloudy or clear, or the position of clouding point or melting point (referring to Table 1), which can be obtained by the first derivative method similar to that used for the salt-free sample. It is found that the position of a transmission curve depends on the salt concentration. With addition of NaCl, the transmission curve shifts to the left (i.e. lower temperature), The higher the NaCl concentration, the more the curve shifts. This indicates that the addition of NaCl makes the turbidity appear at a lower temperature upon heating, meaning that NaCl displays a typical salt-out effect. As we know,  $\text{Cl}^-$  tends to have a stronger interaction with water molecules than the interaction between water molecules. Thus, some of the original hydrogen-bonding network formed by water is destroyed by the salt and this effect is similar to increasing temperature. The competition for water molecules from NaCl, and the salt-induced destruction of the hydrogen bonds between the MC chains and water cause the decrease of MC solubility in water. As a result, at the same temperature, there are more hydrophobic aggregates of MC in a salted MC solution than a salt-free one, leading to stronger light scattering and lower transmittance as compared at a given temperature. Therefore, the clouding point of a salted sample appears at a lower temperature. The increased salt content results in fewer free water molecules available around MC chains and a stronger

Table 1

Clouding point, DSC peak temperature, and sharp increasing temperature of storage modulus  $G'$  for a 0.03 mM MC aqueous solution without and with NaCl, NaI and NaCl–NaI mixtures upon heating

	MC	NaCl (M)				NaI (M)			NaCl–NaI mixtures <sup>a</sup>		
		0.2	0.4	0.6	0.8	0.2	0.4	0.6	3:1	1:1	1:3
DSC peak temperature, °C	61.1	55.3	50.1	46.8	43.1	63.3	64.8	66.3	54.4	56.9	61.5
Clouding point, °C	62.9	56.0	51.0	49.0	44.0	65.1	66.3	69.0	55.1	58.2	62.9
$G'$ sharp temperature, °C	64.1	58.2	52.9	47.8	44.7	65.4	67.8	69.9	56.7	60.1	64.5

<sup>a</sup> The total salt concentration is fixed at 0.4 M.

hydrophobic environment for MC, which causes the turbidity curve to shift further to the left as shown in Fig. 3.

On the other hand, NaI shows an opposite effect from that of NaCl, i.e. the turbidity curve of MC solution with NaI appears to the right of the salt-free one as illustrated in Fig. 4. In the presence of NaI, the sample shows less turbid at the same temperature and the clouding behavior tends to be delayed. It is understood that  $I^-$ , classified as a typical salt-in salt, exhibits a weak hydration ability in water. In an aqueous solution of MC, these  $I^-$  ions behave like hydrophobic particles or an independent solvent besides water in the solution. It seems that MC chains are dispersed by big and hydrophobic-like  $I^-$  ions in the solution, so that there are fewer chances for MC chains to meet to associate or interconnect. Thus, at a given temperature it is more difficult for MC to form hydrophobic aggregates, resulting in less turbidity and a higher clouding point and melting point (referring to Table 1).

The turbidity curves for the MC solutions with a NaCl–NaI salt mixture are presented in Fig. 5. The total salt concentration of the salt mixture is 0.4 M for every solution to ensure that the different effects of salts are only due to varying salt ratio rather than the salt concentration. In Fig. 5, the curve of the pure salt-out solution (i.e. 0.4 M NaCl) appears on the leftmost side with the lowest clouding point.

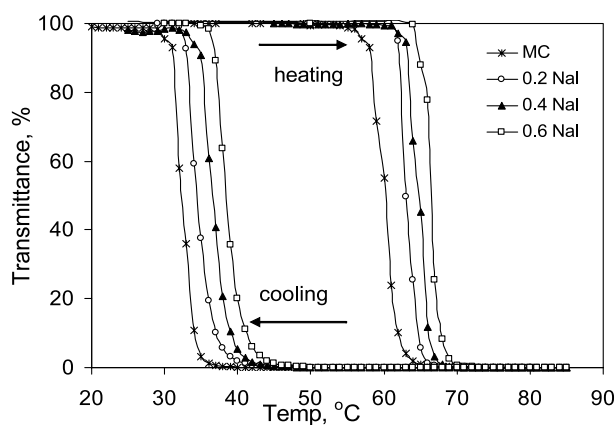


Fig. 4. Turbidity behavior of MC solutions with various concentrations of salt-in salt (NaI) in the thermal cycle at a wavelength of 500 nm.

With increasing NaI content in the salt mixture, the curve shifts smoothly to higher temperature along the temperature axis, until ending at the pure salt-in one (i.e. 0.4 M NaI). The salt-out effect of the salt mixture decreases gradually with reducing NaCl or increasing NaI content in the salt mixture. It seems that the component (NaCl or NaI) in the salt mixture delivers its effect individually and independently, like an acid–base reaction process. The  $Cl^-$  ions in the solution tend to destroy the cage like structures between MC chains and water molecules, increasing the hydrophobicity of MC in water. The  $I^-$  ions, on the other hand, tend to disperse the MC chains, preventing them from association or interconnection, so as to increase the solubility as well as the stability of MC in water. Thus, the solubility of MC in water is modified by a combined effect of salt-out and salt-in after the new balance is established. Therefore, the influences from  $Cl^-$  and  $I^-$  on the gelation of MC are independent of each other.

The clouding points in the heating process for the MC solutions with the salt mixtures are given in Table 1 and further plotted in Fig. 8 against the molar fraction of NaI in the salt mixture. The thermal and rheological temperatures shown in Table 1 and Fig. 8 will be discussed later. From the

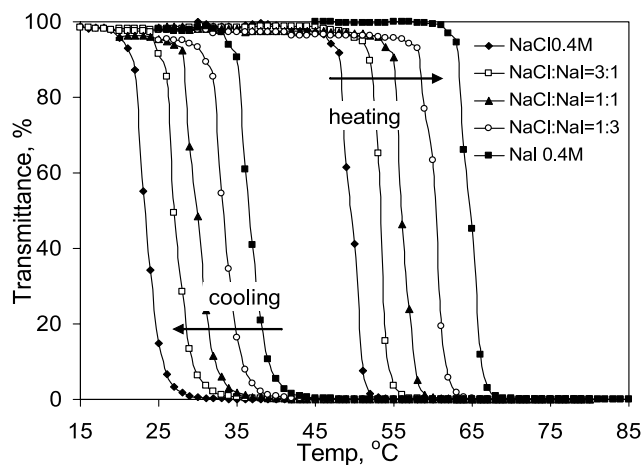


Fig. 5. Turbidity behavior of MC solutions with different ratios of NaCl–NaI salt mixtures during heating and cooling at a wavelength of 500 nm.

results, it is found that a linear relationship exists between the clouding points and the NaI ratio, which can be expressed by the following equation:

$$T_p = m_1 T_{p1} + m_2 T_{p2} \quad (1)$$

where  $T_p$ ,  $T_{p1}$  and  $T_{p2}$  are the peak temperatures for the MC solutions with a salt mixture, NaCl and NaI, respectively, and  $m_i$  represents the molar fraction of each salt component (i.e. NaCl or NaI) in the salt mixture. At the total salt concentration of 0.4 M,  $T_{p1}$  and  $T_{p2}$  are 51.0 °C (NaCl) and 66.3 °C (NaI), respectively, as determined by the clouding point. The excellent fitting of clouding points with Eq. (1) indicates that a linear rule of mixing is valid for the MC solution mixed with the salt mixture. From this linear rule of mixing and the turbidity studies on the mixed-salt series, it is confirmed that the effect of salts on MC gelation depends purely on the salt type and its concentration, and the gelation mechanism involved in MC is similar. A salt-out salt or a salt-in salt can cause MC to gel at a lower or higher temperature by increasing or decreasing the hydrophobicity of MC in water, but the salt itself is not involved in the formation of a gel network. In addition, as we found previously, a salt may slightly affect the gel strength due to an enhanced or reduced hydrophobicity of MC [17].

Although all the above-described turbidity properties are completely thermoreversible, the reversibility has to trace out a hysteresis loop from heating to cooling for any samples (without or with salts) studied. Since, the hydrophobic association of MC occurs in the heating process while the hydrophobic dissociation of MC does in the subsequent cooling process, which are basically not changed by addition of a salt, the hysteresis loop is considered to be due to the kinetics of association and dissociation of MC in water. A delay is involved in the dissociation of the gel network of MC formed in the heating process, which results in the formation of the hysteresis loop. Thermodynamically, one may consider that there are two physical reactions with different reaction constants for the association and dissociation, respectively. The addition of a salt-out salt, a salt-in salt, or a salt mixture only causes a shift of the hysteresis loop to left, right, or between, depending on the salt type, concentration, and composition of the salt mixture. However, a salt or a salt mixture does not really affect the pattern of the hysteresis loop. The effect of heating and cooling rates on the hysteresis was not studied in this work. Since, both the association and dissociation of MC are the kinetic processes, it is expected that the hysteresis will be rate-dependent.

### 3.3. Thermal and rheological behaviors

The clouding behavior of MC with or without salts on gelation can be further supported by the corresponding microthermal and rheological measurements at the same rate of heating and cooling in the similar temperature range.

The micro calorimetric results for the salt-free MC aqueous solution (0.03 mM) and MC solutions with 0.4 M NaCl and 0.4 M NaI, respectively, during a thermal cycle are given in Fig. 6. It is shown that in the heating process, an endothermic sharp peak appears in each curve. On the other hand, a broad exothermic peak is observed in the subsequent cooling process, which is also featured with a shoulder or a secondary peak at the higher-temperature side. The peak temperature in heating is defined as the sol–gel transition temperature, while the primary peak temperature in cooling is defined as the gel–sol transition temperature. The integrated area under the heating peak is assumed as the total enthalpy change during the thermally-induced gelation, which is also the energy needed to destroy the hydrogen bonds between MC chains and water molecules so as to undergo the hydrophobic association. These endothermic peaks in the micro thermal curves correlate well with the narrow temperature ranges in the turbidity curves. Due to the salt-out effect of NaCl, the DSC curve appears at the lower temperature with a bigger enthalpy change, while the NaI shifts it to the right along the temperature axis, exhibiting a typical salt-in effect on gelation.

Fig. 7 shows the temperature dependence of storage modulus ( $G'$ ) during heating. Again, the samples of 0.03 mM MC, MC with 0.4 M NaCl and 0.4 M NaI were

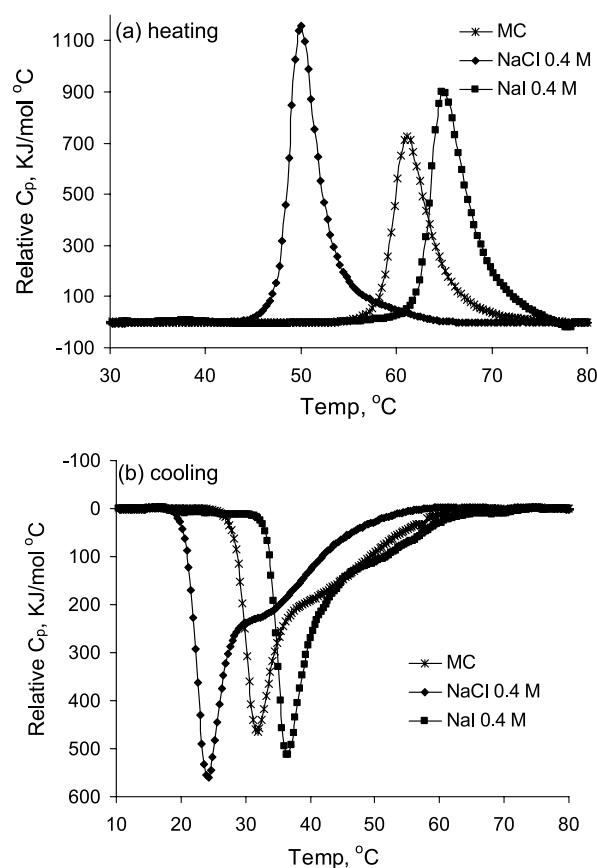


Fig. 6. Relative thermal capacity  $C_p$  for 0.03 mM MC solutions each containing 0.4 M NaCl, and 0.4 M NaI during (a) heating and (b) cooling.

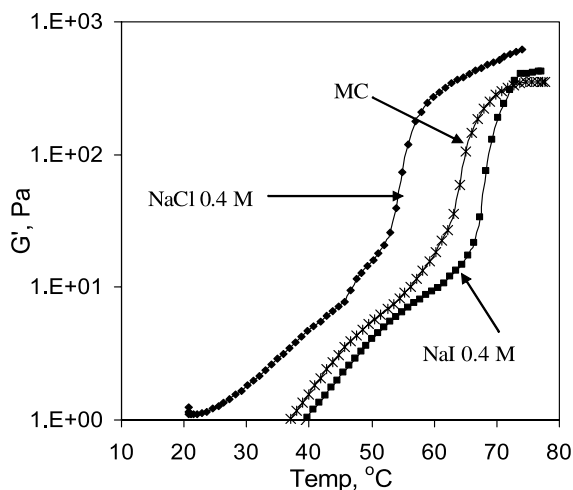


Fig. 7. Storage modulus  $G'$  for 0.03 mM MC aqueous solutions without salt, with 0.4 M NaCl and with 0.4 M NaI as a function of temperature in the heating process.

chosen as representatives. Each curve of  $G'$  follows a similar pattern. It grows gradually at low temperatures, and then increases rapidly within a narrow temperature range until a near plateau is eventually reached. The  $G'$  plateau proves that an elastic gel network structure is formed through the heating process. The temperature at which a sharp increase of  $G'$  occurs is defined as the sol–gel transition temperature from the viscoelasticity point of view. In the presence of NaCl, the  $G'$  curve shifts to the lower temperature, proving that NaCl promotes the sol–gel transition of MC. At the same time, the plateau of  $G'$  curve increases with the adding of NaCl, indicating that the gel is strengthened due to a stronger hydrophobic association induced by NaCl. Different from NaCl, the  $G'$  curve for NaI shows the salt-in effect but a relatively weak effect on the sol–gel transition. As a result, a higher temperature is required MC to gel when NaI is added.

Compared to the thermal graphs for the same solutions, it is obvious that the sharp decrease of light transmittance in Fig. 1, the endothermic peak in Fig. 6, as well as the rapid increase of  $G'$  in Fig. 7 fall into a similar narrow temperature range, which all represent the sol–gel transition of MC as a result of heating. In other words, the turbidity property of MC with or without salts is well supported by the thermal and the rheological behaviors. The three critical temperatures characterizing the different behaviors are listed in Table 1. They are the clouding point, determined by derivative of absorbance, the peak temperature in a micro DSC curve and the temperature at which a sharp increase in  $G'$  occurs, respectively. As shown in Table 1, these temperatures for the same sample are close, although the exact values may not be the same because of the differences in methodology and sensitivity among the three methods. The data in Table 1 are plotted in Fig. 8.

From Table 1 or Fig. 8, it is interesting to note that although there is an exception (NaCl 0.6 M) the critical

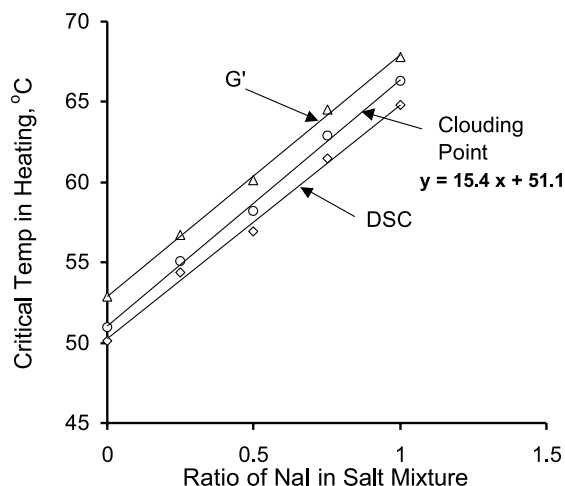


Fig. 8. Critical temperatures of 0.03 mM MC solutions containing NaCl–NaI salt mixtures during heating for three methods as a function of NaI fraction.

temperature of gelation always follows the order:  $G'$  sharp increasing temperature > clouding temperature > DSC peak temperature. Although we can consider that the order is caused by the differences in methodology and sensitivity among the three methods, here we like to propose a mechanism, which can better explain the results. It is considered that the order might be due to the procedure or sequence of MC gelation, in which the heat absorption occurs first to cause the destruction of the hydrogen bonds between MC and water and the exposure of hydrophobic groups of MC for the formation of hydrophobic aggregates, followed by the light scattering for the turbidity caused by the existence of hydrophobic aggregates. As a third step, the connection of these aggregates results in the sharp increase in  $G'$ , eventually leading to the formation of a gel network. Therefore, in a heating process, the  $G'$  sharp increasing temperature should appear later than the critical turbidity temperature, and the critical turbidity temperature should happen later than the heat absorbance measured by DSC. Nevertheless, the slight difference among the three methods does not change the basic feature of the salt-out effect caused by NaCl or the salt-in effect by NaI.

Another important observation from the critical temperatures of gelation obtained by these three methods is that the linear rule of mixing is applicable to each measurement as shown in Fig. 8, which follows nicely the Eq. (1) but with the slight different values of  $T_{p1}$  and  $T_{p2}$ . From Table 1, we can find the values of  $T_{p1}$  and  $T_{p2}$ . For example,  $T_{p1}$  varies from 51.1 °C (from cloud point), 50.1 °C (from DSC) to 52.9 °C (from  $G'$ ). The peak temperature in the DSC heating curve, the sharp increase temperature for  $G'$  and the clouding point during heating are all, respectively, a linear function of NaI fraction in the NaCl–NaI salt mixture, although the three trend lines do not completely overlap due to the different methodologies as mentioned before.

#### 4. Conclusions

The optical transmittance of MC aqueous solutions with and without salts was measured to study the effect of salts on the sol–gel transition of MC as a function of temperature. The turbidity measurement is proved to be an effective tool to characterize the development of hydrophobic aggregates of MC in the solution and the formation of a gel network structure. The clouding point and melting point during the gelation and degelation are defined using the derivative of absorbance. For the MC solutions added with a salt mixture, when the total salt concentration was fixed at 0.4 M, the critical temperatures of gelation determined by the three methods (i.e. clouding point, DSC, and rheology) are all a linear function of salt ratio, respectively. Thus, the linear rule of mixing is valid no matter what method is used to determine the sol–gel transition temperature. At the same time, the effects of salts in the mixture are independent of individual salts. The clouding behavior observed is excellently supported by the thermal and rheological properties.

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