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EFFECT OF SDS ON THE GELATION OF HYDROXYPROPYLMETHYLCELLULOSE HYDROGELS

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Thermal behavior of aqueous hydroxypropylmethylcellulose (HPMC)/surfactant mixtures was studied in the dilute concentration regime using micro-differential scanning calorimetry (DSC). The surfactant used was sodium *n*-dodecyl sulfate (SDS). The heat capacity of HPMC gel with various concentrations of SDS was much higher than that of the pure HPMC gel. The addition of SDS at different concentrations showed dissimilar influences on the gelation of HPMC; SDS at lower concentrations (≤6 mM) did not affect gelation temperature significantly except for enhancing the heat capacity whilst SDS at higher concentrations (≥6 mM) not only resulted in the gelation of HPMC at higher temperatures but also changed the pattern of the gelation thermograph from a single mode to a bimodal. On the basis of the observed thermal behavior of HPMC/SDS systems, the mechanism behind the sol–gel transition was discussed in terms of the properties of the surfactant and their influences on the extent of polymer/surfactant binding and polymer/polymer hydrophobic association. Gelation kinetics was analysed using the results from the DSC measurements. The kinetic parameters were determined.

Keywords: *gelation kinetics, hydrogel, hydrophobic association, hydroxypropylmethylcellulose, surfactant*

Introduction

The behaviour of aqueous mixtures of cellulose derivatives and surfactants has gained considerable interest because of their use in a wide range of applications in pharmaceuticals, cosmetics, and food industry [1, 2]. It was found that gelation of cellulose derivatives such as methylcellulose (MC), carboxymethylcellulose (CMC) and hydroxypropylmethylcellulose (HPMC) in aqueous solutions occur under isothermal and non-isothermal conditions [3–6]. The resulting material known as hydrogel holds large quantities of water within its microscopic network and can be used as microscopic sponges or systems that retain and deliver diverse chemical substances [7]. The addition of surfactant, based on its strong tendency to self-aggregate, affects the behavior of cellulose derivatives with temperature changes [1, 8]. Based on the hydrophobic interaction between hydrocarbon chains, surfactant molecules in aqueous environment tend to self-aggregate. The resulted aggregates easily interact with polymer promoting the integration between polymer chains [8, 9].

Hoffmann *et al.* studied the effect of sodium dodecylsulfate (SDS) and sodium tetradecylsulfate (STS) on the gelation phenomena of hydroxyethyl cellulose (HEC) and modified HEC samples with cationic groups (cat-HEC) or a cationic and hydrophobic group (cat-HMHEC) [10]. HEC was observed to become gel at a temperature lower than 50°C and at minimum concentration of 5% whilst cat-HEC reached the gel state at 4% concentration and the hydrophobic poly-electrolytes were not water soluble when its concentration was higher than 3%. By investigating similar system, Kastner *et al.* reported that on addition of an oppositely charged surfactant the modified HEC solutions showed similar phase behavior of associative phase separation at certain concentrations of surfactant followed by resolubilization with excess surfactant concentrations [11]. The cationic and hydrophobic parts of the modified HEC interacting synergistically with the anionic surfactant molecules resulted in stronger viscoelastic properties than for only cationic HEC. Based on the works of Evertsson and Nilsson, hydrophobically modified ethyl hydroxyethyl cellulose (HM-EHEC) would self-associate and form polymeric micelles in semi-dilute solutions [1]. Significant increase in microviscosity and decrease in micropolarity were observed upon successive addition of SDS. A minor non-cooperative SDS binding to HM-EHEC started from low concentration of SDS (<5 mM) followed by a highly cooperative binding region at SDS concentration ≥5 mM.

The tendency of oppositely charged surfactants and polyelectrolytes to bind together is quantified by the critical aggregation concentration (CAC) at which surfactant molecules begin to aggregate. The strong surfactant/polyelectrolyte interaction may lower the CAC values and overcome the solubility of both components, resulting in the formation of gel due to

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associative phase separation [12]. The gelation was observed to occur as the surfactant diffused into the dispersed polyelectrolyte drops [13]. On the contrary, no interactions would occur in ionic surfactant/nonionic polymer system until the surfactant concentration reached the CAC value [8]. After reaching CAC, free ions of the surfactant start to bind to the polymer through adsorption or cluster formation until the saturation of polymer molecules with surfactant. It is supposed that the nonionic polymer will change into a polyelectrolyte-like polymer when an ionic surfactant adsorbs onto the polymer via its hydrophobic tail. The electrostatic repulsions between ionic heads of the surfactant molecules will result in conformational changes of the polymer molecule. By investigating the gelation of EHEC in presence of a cationic surfactant cetyltrimethylammonium bromide (CTAB), Bystrom *et al.* reported that a coil expansion occurred with increasing temperature due to the enhanced binding of CTAB to EHEC in a dilute solution (0.15%) whilst the mesh size became smaller in a semi-dilute solution because of the progressively stronger tendency of the system to create physical cross-links [14].

Study of gelation kinetics of various materials has been carried using the results from DSC, Rheometer, and light scattering. Bohidar and Jena reported the gelation kinetics of dilute gelatin based on DSC and static light scattering measurements [15]. The enthalpy of the gel melting, the gelation temperature, and the Flory–Huggins interaction parameter were determined. The sol–gel transition path for gelatin was supposed to include three distinct steps-monomer aggregation, coil–single–helix transition and single–helix–triple–helix transition followed by gelation. Alonso *et al.* studied the gelation kinetics of lignin-phenolic resol resin [16]. The kinetic parameters, i.e. the activation energy and the pre-exponential factor, were determined using different isoconversional methods and the results from isothermal gelation. The activation energy was found to be strongly dependent on the degree of gelation. Guo *et al.* investigated the gelation kinetics of modified scleroglucan carrying various fractions of reactive aldehyde groups in the side-chains, scleraldehyde and chitosan by examining the dynamic viscoelastic properties [17]. A maximum gelation rate was attained at a pH value of 7. A change from entropy-dominated elasticity to enthalpy-dominated elasticity and a shift from $\Delta G'/T>0$ to $\Delta G'/T<0$ (where $\Delta G'/T$ indicates the ratio of Gibb's free energy to temperature for the sample) were observed when the crosslink density increased.

In this paper, the effect of SDS on the thermal behavior of HPMC hydrogels was investigated. The mechanism behind the gelation of HPMC/SDS system was discussed in terms of the properties of the surfactant and its influences on the extent of polymer/surfactant binding and polymer/polymer hydrophobic association. The kinetics of gelation for HPMC hydrogels with different concentrations of SDS was investigated.

Theoretical background

The degree of conversion, α_i, represents the fraction of gel in the aqueous system at time t_i and can be evaluated in dynamic runs as the ratio between the heat released, $(\Delta H)_{ti}$, up to a time t_i and the total heat of the reaction, $(\Delta H)_0$ [16]:

$$\alpha_i=\frac{(\Delta H)_{ti}}{(\Delta H)_0} \tag{1}$$

The rate of gelation, defined as $(\mathrm{d}\alpha/\mathrm{d}t)_i$, is determined by differentiating Eq. (1). Thus, numerically it will be the peak height $(\mathrm{d}H/\mathrm{d}t)_i$ at time t_i divided by the total heat of the gelation, $(\Delta H)_0$; thus:

$$\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)_i=\frac{(\mathrm{d}H/\mathrm{d}t)_i}{(\Delta H)_0} \tag{2}$$

For the gelation under non-isothermal conditions, in particular at a constant rate of heating whereby the isothermal effects are negligible, the degree of conversion from solution to a gel state (alternatively, the degree of gelation) may be determined with T as variable; thus:

$$\alpha_i=\frac{(\Delta H)_{Ti}}{(\Delta H)_0} \tag{3}$$

where $(\Delta H)_{Ti}$ is the heat released at temperature T_i. Correspondingly, the rate of gelation, $(\mathrm{d}\alpha/\mathrm{d}T)_i$, may be calculated numerically as:

$$\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_i=\frac{(\mathrm{d}H/\mathrm{d}T)_i}{(\Delta H)_0} \tag{4}$$

where $(\mathrm{d}H/\mathrm{d}T)_i$ is the peak height of the thermogram at temperature T_i.

A popular kinetic model from Sourour and Kamal as in Eq. (5) has been earlier used to describe the isothermal gelation kinetics [18]:

$$\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)_i=(k_1+k_2\alpha_i^m)(1-\alpha_i)^n \tag{5}$$

where k_1 and k_2 are temperature-dependent rate constants and m and n are empirical constants. For non-isothermal gelation process, Eq. (5) may be revised as:

$$\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_i=(k_1+k_2\alpha_i^m)(1-\alpha_i)^n \tag{6}$$

Based on the fact that the gelation rate is zero at the beginning of the heating process, the value of k_1 would have to be zero. Thus, a simplified expression for non-isothermal gelation taking place at a constant rate of heating is:

$$\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_{\mathrm{i}} = (k\alpha_{\mathrm{i}}^{\mathrm{m}})(1-\alpha_{\mathrm{i}})^{\mathrm{n}} \qquad (7)$$

where k is the rate constant for the gelation process.

Experimental

Materials

The HPMC used in this work was purchased from Sigma-Aldrich. The specifications provided by the manufacturer indicate that the HPMC has a molecular mass of 86 000 g mol^{-1} and the viscosity of a 2 mass% solution is 4 000 cps at 20°C. The average degrees of substitution of methyl and hydroxypropyl groups are 1.8–2.0 and 0.2, respectively. HPMC was dried at 60°C overnight under vacuum and stored in a desiccator before use. Sodium *n*-dodecyl sulfate (SDS) was also purchased from Sigma-Aldrich. The deionized (DI) water was from Alpha-Q Millipore water purification system.

Sample preparation

A 1.0 mass% HPMC solution was prepared by dispersing weighed HPMC powders into DI water. The stock solution was stored in a refrigerator (4°C) for 24 h until a homogeneous and transparent solution was obtained. Weighed surfactant was then added into the HPMC solutions and stirred overnight. All the samples were stored in a refrigerator before measurement.

Microthermal measurement

A differential scanning calorimeter (VP-DSC MC-2 microcalorimeter, MicroCal Inc.) was used to study the thermal behavior of the HPMC/SDS solutions. The sample solution (0.5158 cm^3) and an equal amount of solvent as a reference were hermaetically sealed into the sample cell and the reference cell, respectively. The measurement included heating the sample from 20 to 90°C and subsequently cooling to 20°C at the same scanning rate of 1°C min^{-1}. The values of relative heat capacity, C_p, were normalized for 1 dm^{-3} of sample volume by multiplying the original data by a factor of 1000 cm^3/0.5158 cm^3, where 0.5158 cm^3 was the sample volume. DI water was used as reference for all the microthermal measurements. Before each test, the sample and reference cells were thoroughly cleaned.

Results and discussion

Curves from DSC

The relative heat capacity profiles depicting thermal behavior of HPMC/SDS solutions with different SDS concentrations determined by means of micro-DSC during a heating process are shown in Fig. 1. In absence of SDS, the HPMC solution showed a small peak with a peak temperature of 61°C. With addition of SDS, either the height of the peak or the position of the peak was altered. As seen in Fig. 1, at SDS concentration of 2 mM, the HPMC solution showed a DSC profile that was distinctly different from that for the pure HPMC solution. The peak of the profile shifted slightly to a lower temperature. A similar shift in the peak was observed in the case of the SDS concentration of 4 mM (the plot is not included in Fig. 1 to maintain clarity). Thus, it may be said that the addition of SDS at low concentrations (i.e. 2 and 4 mM) had the salt-out effect on the gelation of HPMC, which essentially means the gelation of these SDS/HPMC solutions occurred at lower temperatures. This phenomenon is consistent with that observed for a SDS/MC system by others [19]. The relative heat capacity for the sol–gel transition processes significantly increased as compared with the pure HPMC solution. When the SDS concentration was increased to 6 mM, the peak of the corresponding curve appeared at nearly the same temperature as that for the pure HPMC solution but the onset of the sol–gel transition was observed to occur later. Based on these observations, it is very clear that a SDS concentration of 6 mM had a more significant and different influence on the gelation of HPMC. At SDS concentrations higher than 6 mM, the sol–gel transition started at even higher temperatures with the peak shape of

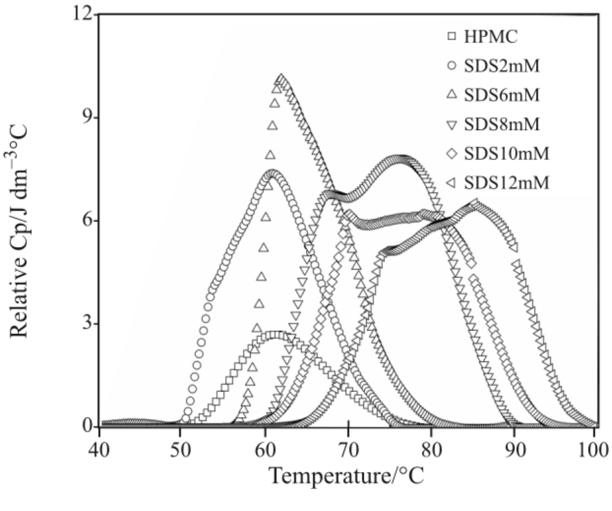

Fig. 1 Relative heat capacity as a function of temperature for 1.0 mass% HPMC solutions with different concentrations of SDS

corresponding curves changing from a single mode to a bimodal. Each curve covered a wider range of temperature with reduced height of the first peak.

Effect of SDS on HPMC gelation

Based on the DSC observations, a schematic diagram of the interaction between HPMC and SDS as well as the gelation of HPMC/SDS system is constructed and shown in Figs 2a–d. Below 6 mM concentration, SDS existed as dissociative ions and not any integrates came into being (Fig. 2a). Under a HPMC concentration of 1.0 mass%, there are negligible interactions between SDS and HPMC when SDS concentration is between 0 and 6 mM. Therefore, the presence of SDS in this concentration range did not significantly affect the gelation of HPMC; the water cages were broken upon heating and sol–gel transition took place owing only to the hydrophobic association of HPMC chains. The relative heat capacity, C_p, only increased quantitatively due to the presence of SDS. When the concentration of SDS was higher than 6 mM, the gelation phenomenon of HPMC was obviously affected. Thus, a concentration of 6 mM for SDS can be considered as the CAC value in presence of HPMC. After reaching the CAC value, binding of SDS to HPMC occurred either through adsorption or through cluster formation with HPMC (Fig. 2b). For a binary SDS/water system, it is well characterised that the critical micellization concentration (CMC) of SDS is around 8 mM. Since the interaction between SDS and HPMC molecules would start at a SDS concentration of 6 mM, the formation of SDS/HPMC complex is energetically more favorable than the formation of SDS micelles. Between CAC (6 mM) and CMC (8 mM), SDS molecules continually bound to the available sites of HPMC either as monomeric surfactants or small micelles of low aggregation number.

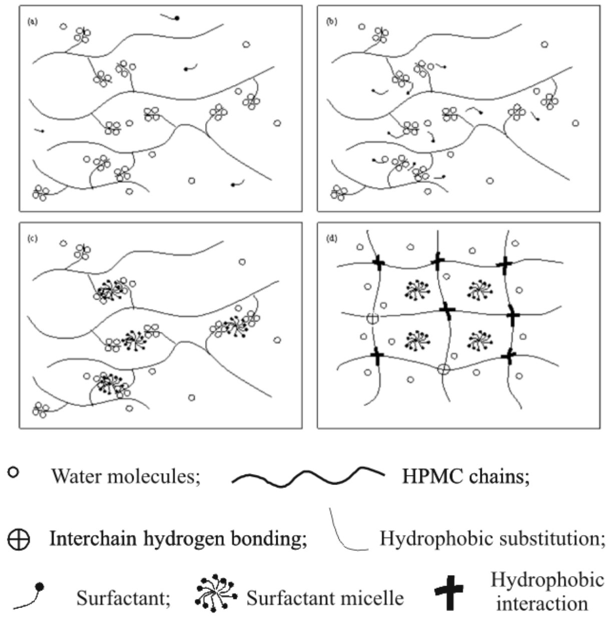

Fig. 2 Schematic diagram of the interaction between HPMC and SDS: a – SDS concentration lower than 6 mM; b – SDS concentration between 6 and 8 mM; c – SDS concentration higher than 8 mM and d – the network structure of HPMC gel

Above 8 mM, micelles of larger aggregation number began to form around the side groups of HPMC chains (Fig. 2c). The SDS–HPMC interaction was intermolecular in nature, i.e. one bonded micelle was shared by two or more HPMC molecules creating a three-dimensional network. This binding occurred at a temperature lower than the gelation temperature and continued until the saturation of HPMC molecules with SDS as evidenced by measuring the conductivity of such a system [8]. With continued heating, the binding continued and hydrophobic association between neighboring HPMC chains progressed. The SDS units gradually moved away from the side chains of HPMC along with the breaking of the water cages. During the heating process, the breaking away of both the surfactant micelles and water cages needed more energy. Consequently, the endothermic peaks appeared on curves at higher temperatures. After the SDS micelles and water cages were removed, hydrophobic groups of HPMC were exposed and intermolecular association occurred to form new junctions for the gel network. This delayed gel formation attributed to the second peak in the thermograms.

Kinetic analysis of gelation

The gelation kinetics of HPMC with and without surfactant SDS was studied using the data from DSC measurements. Figure 3 shows the values of the degree of conversion (determined using Eq. (3) and the data presented in Fig. 1) for HPMC samples with or without SDS. The sol–gel transition of the pure aqueous HPMC hydrogel started at around 55°C. With the increasing

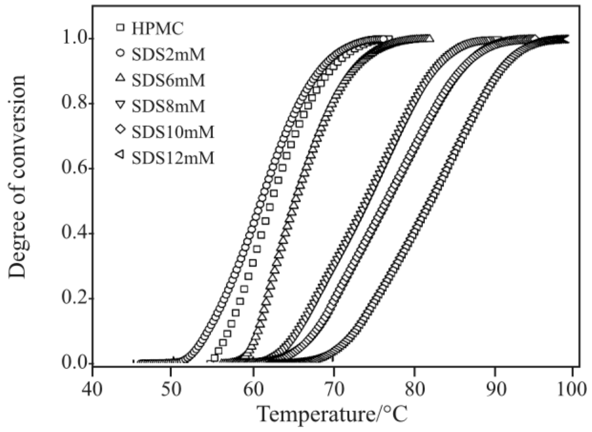

Fig. 3 Effect of SDS on the gelation of 1.0 mass% HPMC hydrogel

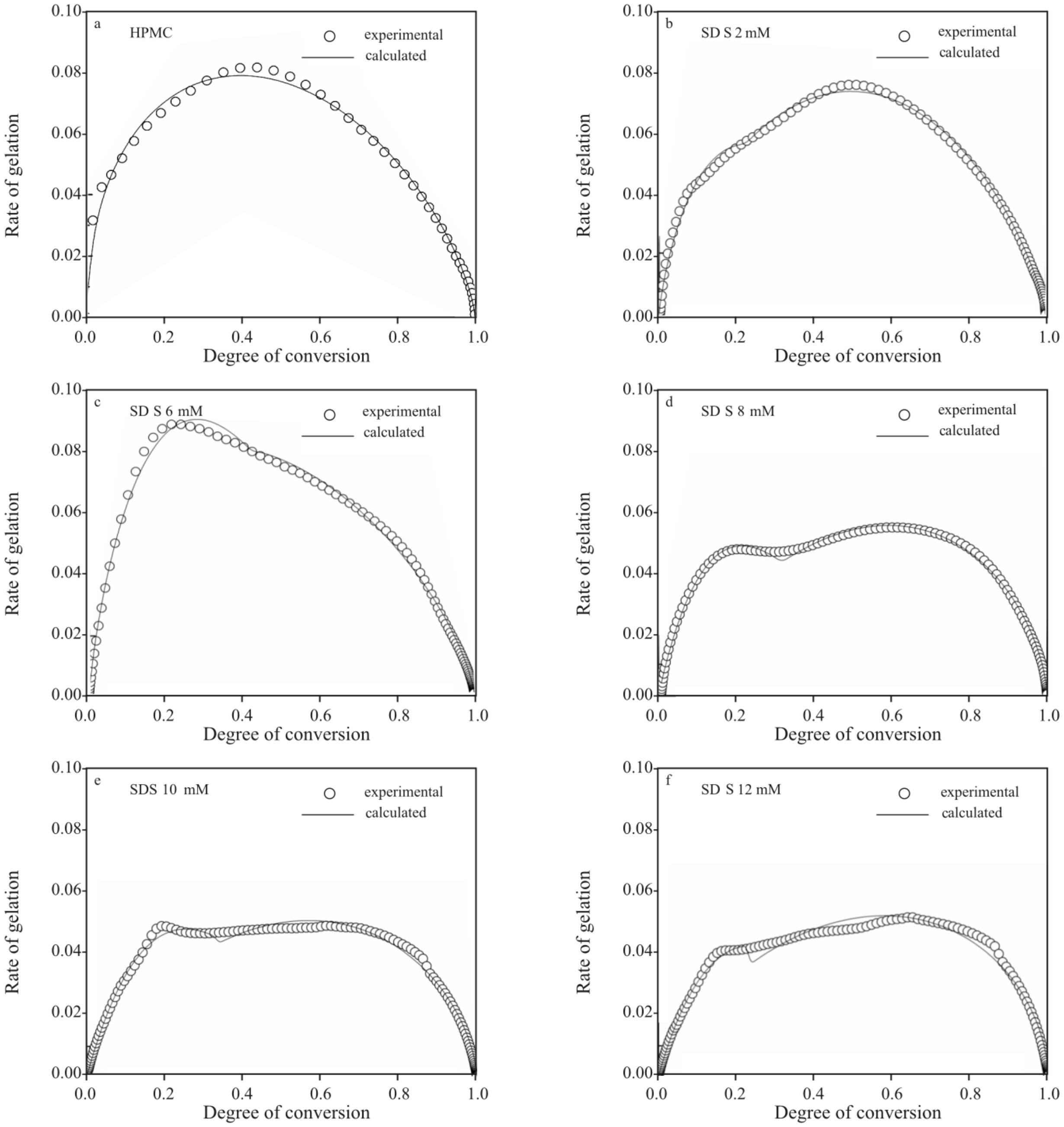

Fig. 4 Effect of SDS on the gelation kinetics for 1.0 mass% HPMC hydrogel

temperature, the degree of conversion increased sharply and the gelation completed at 77°C. With the addition of SDS at a low concentration, i.e. 2 mM, the curve for the degree of conversion shifted to the left hand side with a lower slope as compared to that of HPMC solution without SDS. The sol–gel transition for aqueous HPMC/SDS (2 mM) system was observed to occur at a temperature of 51°C. At a higher SDS concentration of 6 mM, the curve for the degree of conversion shifted to the right hand side with its slope comparable to pure HPMC solution. The sol–gel transition of the aqueous HPMC/SDS system with 6 mM SDS occurred at a higher temperature of about 58°C. Further increase in the SDS concentration resulted in continuous shifting of the degree of conversion curve with decreasing slope.

In Figs 4a–f, the symbols are the experimental data representing the rate of gelation $(d\alpha/dT)_i$ as a function of T_i. The kinetic parameters k, m and n were determined by fitting the experimental data presented in Fig. 4 to Eq. (7) using nonlinear regression analysis. For the experimental data showing the effects of SDS at all concentrations, the nonlinear regression was carried out in two steps based on the fact that the corresponding curves had two peaks. The values for all four parameters are tabulated in Table 1. The corresponding curves are shown in Figs 4a–f. One

Table 1 Kinetic parameters (Eq. (7)) for non-isothermal gelation of 1.0 mass% HPMC

SDS concentration/mM	k/min^{-1}		*m*		*n*	
	For peak 1	For peak 2	For peak 1	For peak 2	For peak 1	For peak 2
0	0.17	–	0.46	–	0.69	–
2	0.34	0.20	0.78	0.75	2.66	0.76
6	0.50	0.17	0.79	0.37	2.03	0.71
8	0.48	0.15	0.95	0.90	3.49	0.62
10	0.42	0.13	0.98	0.80	2.87	0.60
12	0.36	0.12	0.95	0.76	2.96	0.55

Table 2 Deviation of calculated rate of gelation from the experimental data

SDS concentration/mM	0	2	6	8	10	12
Deviation	0.00197	0.00161	0.00162	0.00122	0.00119	0.00156

may see that a reasonable mapping of the experimental data was obtained using Eq. (7). The standard deviation of the calculated gelation rate using the rate constant obtained by curve fitting is shown in Table 2. The deviation of the calculated values ranged from 0.00122 to 0.00197, which was very low indicating that the rate constant determined using the model was sufficiently accurate and acceptable. Interestingly, the kinetic rate constant increased from 0.17 min^{-1} to a maximum value of 0.50 min^{-1} with the increasing SDS concentration from 0 to 6 mM. As discussed above, SDS existed as dissociative ions in the aqueous HPMC/SDS hydrogels and no integrates came into being in this concentration range. Such free SDS molecules would attract the water molecules, resulting in increasing hydrophobicity due to these water molecules available for HPMC chains [19]. Therefore, the sol–gel transition during the heating process was accelerated because of the enhanced hydrophobic association of HPMC. At higher SDS concentrations (≥8 mM), SDS micelles as well as HPMC/SDS complexes coexisted in the aqueous HPMC/SDS solution. Upon heating, the moving away of SDS from the side chains of HPMC and the breaking of the water cages corresponded to the first peaks shown in Figs 4d–f. The rate constant for this step decreased from 0.48 to 0.36 min^{-1} with the increasing SDS concentration from 8 mM to 12 mM. With the continued heating, hydrophobic groups of HPMC were exposed and intermolecular association occurred to form new junctions for the gel network. This process corresponded to the second peaks shown in Figs 4d–f, and the rate constant of this process decreased from 0.15 to 0.12 min^{-1}.

Conclusions

The thermal behavior of HPMC hydrogel was influenced with addition of surfactants. With addition of SDS lower than 6 mM, SDS existed as dissociative ions within the solution and the gelation of HPMC/SDS mixtures occurred at lower temperatures as compared to pure HPMC hydrogels. The addition of SDS higher than 6 mM concentrations significantly affected the HPMC gelation; not only the peak shape of curves changed from a single mode to a bimodal but also each curve covered a wider range of temperature with reduced height of the first peak. The reasons for this phenomenon were that SDS molecules would continually bind to the available sites of HPMC chain either as monomeric surfactants or small micelles of low aggregation number when SDS concentration was between 6 and 8 mM. Micelles of larger aggregation number began to form around the side groups of HPMC chains above SDS concentration of 8 mM. Due to the intermolecular nature of the SDS-HPMC interaction, one bonded micelle might be shared by two or more HPMC molecules creating a three-dimensional network. The SDS micelles as well as water cages were removed upon heating the HPMC/SDS mixture to high temperatures, resulting in the exposure of HPMC hydrophobic groups. Therefore, intermolecular association of HPMC chains occurred late and gelation was delayed. A generic kinetics model worked well in describing the gelation kinetics of HPMC/SDS based on the DSC measurements.

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