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THERMODYNAMIC CHARACTERISTICS OF GELATION FOR METHYL-CELLULOSE HYDROGELS

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Methylcellulose (MC) is a thermo-reversible physical hydrogel. This study investigates the thermodynamic characteristics of gelation mechanism for MC. The relative and absolute specific heat capacity values of the hydrogel system were modeled using an empirical formulation to facilitate calculation of thermodynamic parameters. Experiments verifying the assumptions for the model formulation were conducted and are discussed. Parameters such as enthalpy, entropy, and changes in their magnitude as a function of temperature were calculated and their trends were studied. The implications of these observations on the various stages of the gel formation process and the associated mechanisms are evaluated. The studies revealed that the gelation of MC is a temperature-driven process rather than only driven by the heat input, and it attains a state of equilibrium under isothermal conditions. During gelation, the entropy of the overall (MC+water) system increases due to an increase in the disorderliness of the MC system.

Keywords: *DSC, enthalpy, entropy, hydrogel, methyl-cellulose*

Introduction

Hydrogels are three-dimensional network of polymers formed by either chemical or physical cross-linking in water. They play an increasingly important role in biomedical and pharmaceutical applications [1–6]. Many hydrogels are thermo-reversible gels, meaning that they can exist in either liquid or gel form depending on their temperature. Understanding the gelation of thermo-sensitive hydrogels will provide a useful insight in their applications for many important processes, including drug delivery.

Methylcellulose (MC) is a type of thermo-reversible physical hydrogel which is extensively used as thickener or binder in pharmaceutical, ceramic processing and food applications. Numerous studies on the sol–gel transformation process for MC system have been carried out and an explanation for the gelation phenomenon is provided by several researchers including our earlier work [7–12].

At low temperatures, the polar water molecules form cages around the hydrophobic methoxyl groups of MC, causing MC to become soluble. Upon heating, the water cages break to expose the hydrophobic side groups of MC chains, inducing hydrophobic associations and thus gelation. As temperature increases further, more and more hydrophobic aggregates are formed until they join together to develop into a full three-dimensional network. Water molecules are entrapped in the network cells, causing them to enlarge until there is an equilibrium swelling level attained between the osmotic swelling forces and the elastic retraction forces of the network [13]. Upon cooling, it will revert back to the solution state, a process which may be referred as degelation. The gelation properties of MC hydrogels can be substantially altered by the use of additives such as surfactants and salts [14–16]. This is of great interest for manipulating the performance of hydrogels used for biomedical, pharmaceutical, and cosmetic applications.

Based on thermodynamic analysis, sol-gel transformation process will occur only if the free energy of the system decreases, inducing a spontaneous change. The hydrophobic association of MC molecules in water is a thermodynamic process determined by the difference in the Gibbs free energy (ΔG) between the free state and the associative state. During the heating process, heat is absorbed to release the water molecules of the hydrogen bonds that associate water with the MC chains, causing the water molecules to become free and move randomly. The hydrophobic association of MC polymers is then made possible, causing gelation to occur.

In this investigation, the thermodynamic characteristics of MC gelation are studied so as to gain a better understanding on the nature of the gelation process. The changes in enthalpy, ΔH, the changes in entropy, ΔS, and finally the changes in free energy, ΔG are calculated and examined. Since the calculation of these important system parameters depends entirely on the accuracy of DSC measurements of the specific heat capacity of the system, C_p, the experimental trends and

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their modeling are discussed. The validity of the C_p model developed in our earlier work [16] was tested by conducting isothermal DSC measurements on MC solutions. The implications of the changes in the values of ΔH, ΔS and ΔG so determined at various stages of the gelation process are evaluated. It is shown that the gelation of MC is predominantly a temperature-dependent process. The application of the model to pure MC solutions is studied.

Theoretical background

Equation (1) represents the generalized form of our C_p model for MC solutions with salt additives [16].

$$C_p(T-T_p)=\frac{(\lambda_1+\lambda_2)C_{pv1}}{\lambda_1 e^{(T-T_{p1})C_1}+\lambda_2 e^{-(T-T_{p1})C_2}}+ \\ +\frac{(\lambda_3+\lambda_4)C_{pv2}}{\lambda_3 e^{(T-T_{p2})C_3}+\lambda_4 e^{-(T-T_{p2})C_4}} \tag{1}$$

where T_p is defined as the temperature at which the heat capacity for the endothermic curve is at the maximum during gelation. Each of the two expressions in Eq. (1) describes a bell-shape curve. The denominator terms define the progress of the reaction as a function of temperature and depending upon the values of the associated constants control the spread and the shape of the curve. λ_1 and λ_2 are the frequency parameters with the unit 1/K. The terms C_i (i=1, 4) resemble $R/\Delta E$ term in a typical Arrhenius form of reaction kinetics equation, where ΔE is the activation energy (J mol^{-1}) and R the universal gas constant (8.314 J mol^{-1} K^{-1}). This C_p model describes the heat capacity curves for MC systems as superimposition of two bell-shape curves.

The gelation of any thermo-reversible hydrogel is a thermodynamic process as it involves energy exchanges between the gel system and the surroundings, resulting in the sol–gel transition of the system. The change in Gibbs free energy for the system is defined as:

$$\Delta G=\Delta H-T\Delta S \tag{2}$$

where T represents the constant temperature (in Kelvin) of the surrounding in which the reaction is taking place. At constant temperature and pressure, a change is spontaneous only if it is accompanied by a decrease in the free energy (G) of the system. Reactions are considered to be exergonic if G decreases or endergonic if G increases [17]. Reactions are considered in equilibrium if ΔG=0. Entropy, S, is a measure of the disorder in the system. The higher the value of S, the more disorderliness the system possesses. Entropy is a state function; regardless of whether the process is reversible or irreversible, the entropy change between two specified states is the same [17].

When temperature of a system continuously changes at a certain rate, then quantities ΔH and ΔS can be calculated using DSC data respectively as:

$$\Delta H=\int C_p\mathrm{d}T \tag{3}$$

$$\Delta S=\frac{\Delta H}{T}=\int\frac{C_p}{T}\mathrm{d}T \tag{4}$$

The C_p of liquids and solids, in general, depends on temperature. However, the entropy change of an incompressible substance depends on temperature only. Since solids and liquids can be idealized as incompressible as their volumes remain essentially constant during a process, C_p can be treated as a constant at some average value over a given temperature range [18].

Experimental

Materials and methods

Methylcellulose (MC), with the trade name, SM4000, was kindly provided by Shin-Etsu Chemical Co. Ltd. The material specifications indicated that the MC has a mass-average molecular mass (M_w) of 310,000 and an average degree of substitution (DS) of 1.8. MC was dried overnight under vacuum at 60°C and kept in a desiccator before use. The MC solutions were prepared by dispersing the polymer into de-ionized water at 70°C. After being mixed well, it was kept in refrigerator to dissolve MC for at least 1 day to get a homogeneous solution.

DSC data presented in [12], which is the relative thermal capacity, C_p, for the aqueous MC solutions at different concentrations, namely, 0.56, 0.91, 1.53, 1.83 and 2.19 mass%, were obtained using a micro differential scanning calorimeter (VP-μDSC, MicroCal Inc.). A sample solution of 0.5158 mL and an equal amount of de-ionized water as a reference were hermetically sealed into the sample cell and reference cell, respectively. A heating rate of 1.0 K min^{-1} was used during the heating process and DSC curves were recorded in the temperature range of 10 to 85°C. No observation about any phase separation was reported at any of the temperatures.

From the DSC data, gelation of 2.19 mass% MC solution begins at approximately 321 K. For solutions with lower concentration of MC, the onset of gelation is slightly delayed (refer Fig. 1). The C_p values for all cases, however, showed small but negligible fluctuations around zero at the beginning and at the end of the experiments. As such, the base C_p value was set at 321 K to normalize the experimental data. In other words, the onset temperature (T_{on}) is set at 321 K for all the MC solutions. The offset temperature (T_{off}) is determined by the intersection of the base C_p line with the

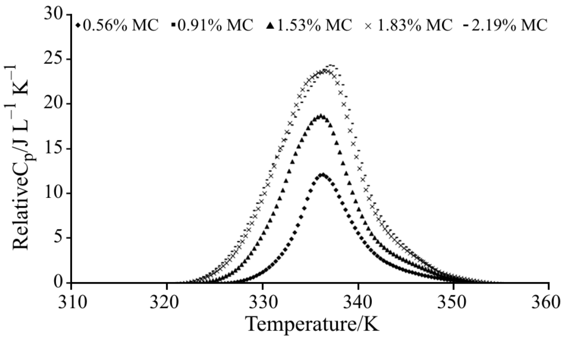

Fig. 1 Plot of heat capacity *vs*. temperature curves obtained after normalizing DSC data measured at 60°C h^{-1} for different MC concentrations

Table 1 C_p curve parameters based on DSC data for 5 different samples of MC hydrogels

MC concentration/ mass%	T_{on}/K	T_{off}/K	T_p/K	ΔH_T/J L^{-1}
0.56	321	353.86	336.23	95.55
0.91	321	351.88	335.58	120.88
1.53	321	353.62	335.97	179.49
1.83	321	354.84	336.71	262.41
2.19	321	353.28	336.86	273.01

DSC curves. The normalized DSC results are shown in Fig. 1. These plots were used to calculate the total heat energy required for gelation, ΔH_T, by summing up the area under the curves. The values of parameters T_{on}, T_{off}, T_p, and ΔH_T are contained in Table 1.

In addition, DSC measurements for the isothermal heating of 0.91 and 1.53 mass% MC solutions at 329 K (56°C) and 337 K (64°C) were carried out to determine if there exists a condition of equilibrium for the MC systems at constant temperatures. Note that the temperatures 329 and 337 K were selected intentionally as they are close to the peak gelation temperature and fell on either side of it on the DSC curve. The results presented in Fig. 2 verify that equilibrium condition did exist, and thus the assumption of equilibrium condition employed in the development of the gelation model for the MC systems is valid.

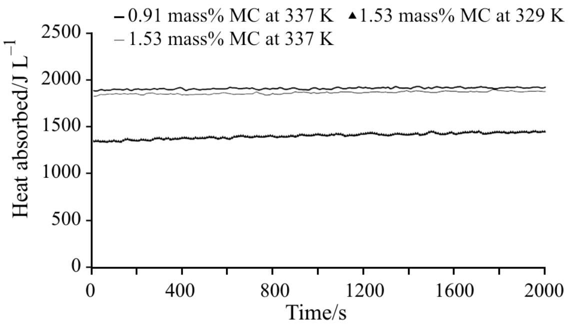

Fig. 2 Plot showing heat absorption under different isothermal conditions by MC solutions as a function of time

Results and discussion

Calculation of thermodynamic parameters and validation of C_p model

For the case of MC system, where C_p values are a strong function of temperature, the enthalpy and entropy changes for any given small temperature range defined from T_{i-1} to T_i can be calculated as:

$$\delta H = \int_{T_{i-1}}^{T_i} C_{p(avg)} \mathrm{d}T \tag{5}$$

$$\delta S = \int_{T_{i-1}}^{T_i} \frac{C_{p(avg)}}{T} \mathrm{d}T = C_{p(avg)} \ln\left(\frac{T_i}{T_{i-1}}\right) \tag{6}$$

where $C_{p(avg)}$ is the specific heat capacity averaged over the temperature range, T_i–T_{i-1}. The scanning temperature interval for the available μDSC data varied from temperature to temperature and also from MC solution to solution, although always less than 0.5 K. Thus, for ease of calculation but without any loss of generality, the C_p model (Eq. (1)) fitted to the DSC data was employed for the calculation of δH and δS values. As the presence of salts in MC solutions has no impact on the patterns of the heat capacity curves [15], Eq. (1) could be employed to obtain an accurate empirical fit for pure MC–water systems. The coefficients for the C_p model for all 5 MC solutions shown in Fig. 1 were obtained using a least-square-error fit method described in [16].

To obtain the δH and δS values for the entire MC hydrogel system (i.e. MC+water), C_p of water had to be added to the normalized DSC data. Thus, Eq. (1) was modified to:

$$C_p(T-T_p) = \frac{(\lambda_1+\lambda_2)C_{p\nu 1}}{\lambda_1 e^{(T-T_{p1})C_1} + \lambda_2 e^{-(T-T_{p1})C_2}} + \\ + \frac{(\lambda_3+\lambda_4)C_{p\nu 2}}{\lambda_3 e^{(T-T_{p2})C_3} + \lambda_4 e^{-(T-T_{p2})C_4}} + C_p(\text{water}) \tag{7a}$$

The specific heat capacity of water over the range between its melting and boiling points (i.e. from 273 to 373 K) given in [19] was employed. The plot for C_p of water as a function of temperature is shown in Fig. 3a; the equation of the best-fit line is determined as:

$$C_p(\text{water}) = 3.893e^{-9}T^4 - 9.396e^{-7}T^3 + \\ + 8.74e^{-5}T^2 - 3.258e^{-3}T + 4.221 \tag{7b}$$

Equation (7b), which is applicable for the temperature range of 273 to 373 K, serves as an empirical fit for ease of computation of various thermodynamic

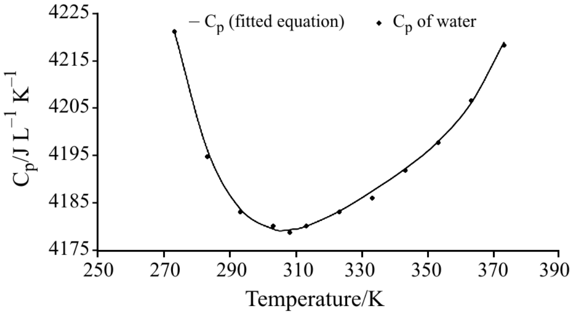

Fig. 3a Plot of heat capacity for 0.0 mass% MC (i.e. only de-ionized water, the reference fluid used) [19]

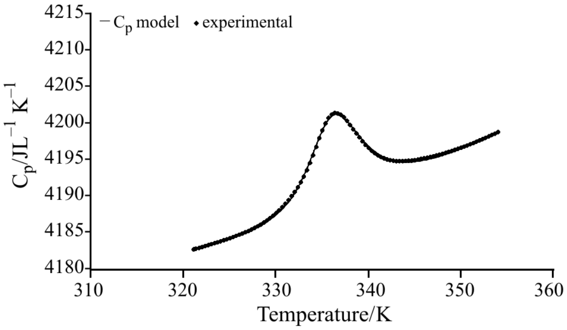

Fig. 3b Plot of heat capacity for 0.56 mass% MC

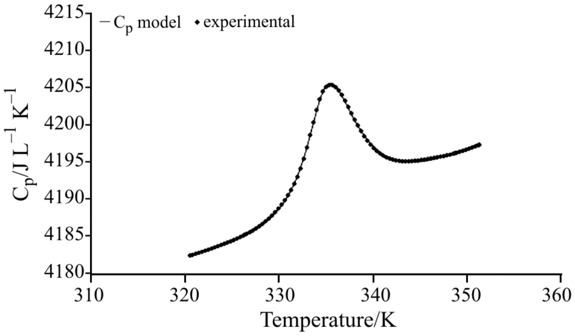

Fig. 3c Plot of heat capacity for 0.91 mass% MC

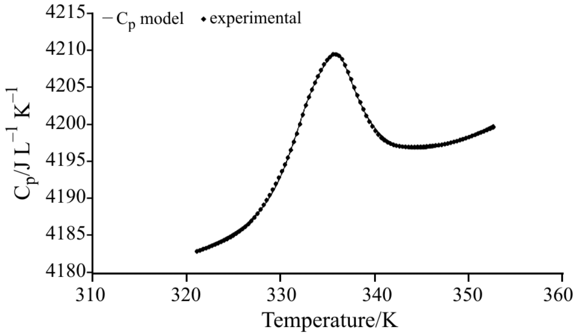

Fig. 3d Plot of heat capacity for 1.53 mass% MC

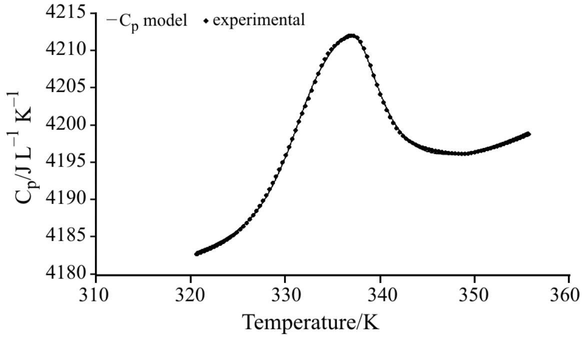

Fig. 3e Plot of heat capacity for 1.83 mass% MC

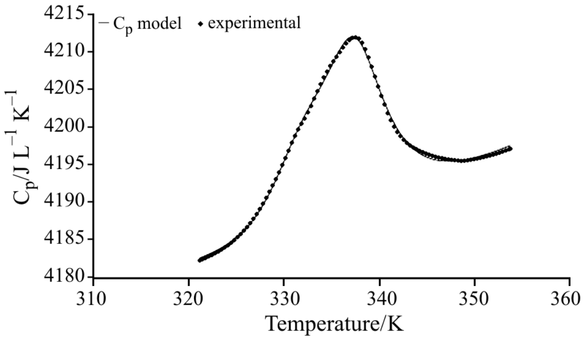

Fig. 3f Plot of heat capacity for 2.19 mass% MC

parameters for the hydrogels. The results of Eq. (7a) and its correlation with the DSC data for all MC concentrations are presented in Figs 3b–f.

With the empirical constants for the C_p model known (Eq. (7a)), δH and δS were calculated for all MC concentrations using a fixed temperature interval (δT) of 0.25 K over the temperature range bound by T_{on} and T_{off}. This temperature interval was selected subsequently after performing a convergence test which revealed that a temperature interval of 0.5 K or less would have no effect on the results obtained. In addition, the cumulative entropy change, ΔS, from T_{on} (n=1) to any given temperature, T_i, is calculated as:

$$\Delta S=\sum_{n=1}^{n=i}\delta S \qquad (8)$$

Figure 4a shows a plot of cumulative change of entropy ΔS *vs*. temperature for 0.56 mass% MC solution. It shows that entropy is monotonically increasing for the temperature range investigated. However, more interesting features can be revealed by calculating the rate of change of ΔS with a change in temperature (i.e. dS/dT) as a function of temperature for the entire system as well as that for water alone. This is plotted in Fig. 4b, which shows that the rate is monotonically decreasing, with the difference between dS/dT of water alone and the entire gelation system highlighted. The dS/dT curves for the rest of the MC solutions are presented in Fig. 5. To verify that the computation did not violate the equilibrium conditions for the whole temperature range, the free energy change at every temperature interval, δG was calculated as:

$$\delta G=\delta H-T_{\mathrm{avg}}\delta S \qquad (9)$$

It may be noted that for Eq. (9), strictly speaking, the temperature should be constant. We employed a small temperature interval, $\delta T=(T_i-T_{i-1})=0.25$ K, and thus with negligible variations of C_p over this temperature range. The use of an average temperature $T_{\mathrm{avg}}=(T_i+T_{i-1})/2$ is a good and acceptable approximation. As expected for the sol–gel transition process, the values of δG for all temperature intervals and MC solutions were close to zero.

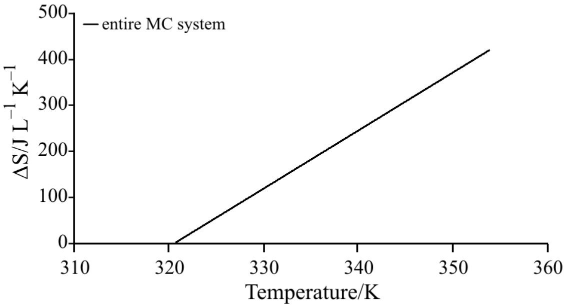

Fig. 4a Plot of cumulative entropy change, Δ*S*, as a function of temperature (with the effect of C_p of water added in) for an aqueous solution of 0.56 mass% MC

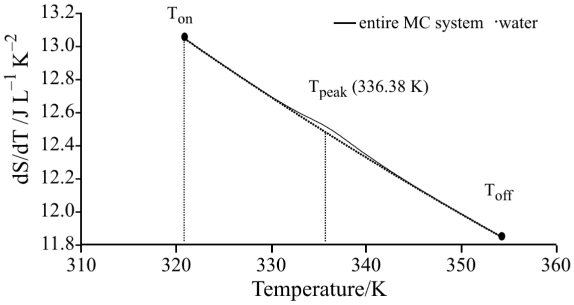

Fig. 4b Plot of d*S*/d*T* with temperature (with water effect) for 0.56 mass% MC

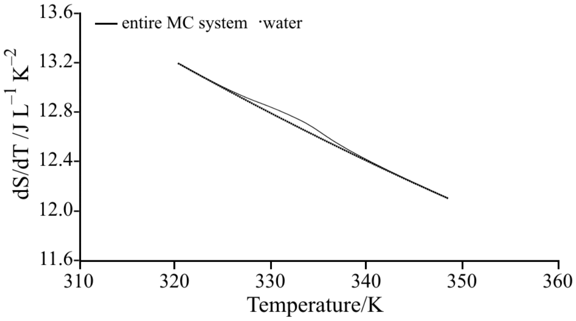

Fig. 5a Heating of 0.91 mass% MC

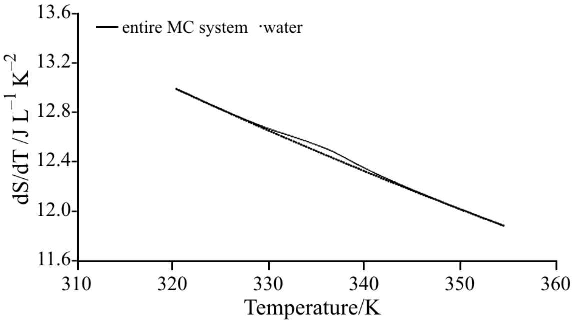

Fig. 5b Heating of 1.53 mass% MC

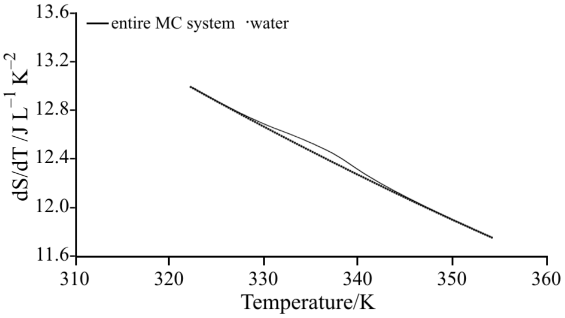

Fig. 5c Heating of 1.83 mass% MC

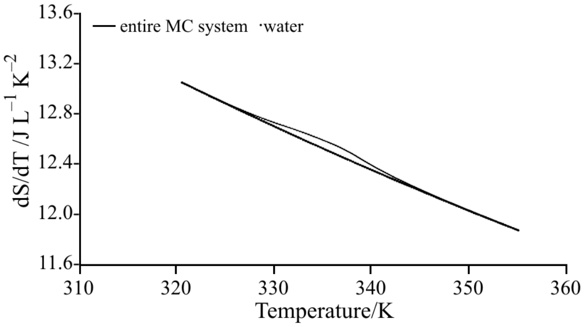

Fig. 5d Heating of 2.19 mass% MC

C_p model and thermodynamic parameters

As seen in Fig. 1 and Table 1, ΔH_T increased with MC concentration as gel formation involved more MC macromolecules with an increase in MC concentration. In conjunction with Fig. 2, and as discussed earlier, the results indicated that gel formation was a temperature-dependent process. Thus, gelation requires both heat input and an increase in temperature.

Table 2 Correlation between C_p model and experimental data

MC concentration/ mass%	Discrepancy between C_p model and experimental data	
	error in ΔH_T/%	error in α_g
0.56	–1.23	0.0032
0.91	0.07	0.0002
1.53	0.58	0.0013
1.83	0.75	0.0013
2.19	0.47	0.0007

As seen in Fig. 3, the simulated heat capacity curves plotted using the C_p model for the whole system (MC and water) represented the experimental DSC data excellently, with insignificant discrepancies as indicated in Table 2. This corroborates the suitability of Eq. (1) for these gel systems.

Figure 4b shows the variation of dS/dT with temperature for 0.56 mass% MC, together with that of the reference fluid (water). It is evident that the change in entropy of water dominates. However, over the gelation region as defined by T_{on} and T_{off}, there is discernible difference between the entire MC system and water, with the rate of change of entropy being slightly higher (more positive) for the entire MC system. This indicates the entire MC system becomes more disorderly as compared with the water alone in the system. With gelation, it is expected that water molecules in the gel system to be more orderly than the water alone (no gel) for a given temperature. Thus, this increase in entropy (disorderliness) over and above that of the water disorderliness with an increase in temperature must come from the MC system. Thus, this slight, but discernable difference between the change in entropy for the entire MC system and water is significant.

This difference could be attributed directly to the gelation mechanism. For the relatively low-temperature activities, the water cages begin to deform and break to expose the hydrophobic regions of MC chains. The ordered state of water molecules and the MC molecules changes to a relatively disordered state, causing the entropy to increase. As the temperature rises further, the disorderliness in the system increases because some energy is utilized in moving the MC chains towards each other. This energy change in MC in water required very small amount of energy (about 12–25 J L^{-1} K^{-1}) as compared to that of water (4179–4221.1 J L^{-1} K^{-1}). This, we believe, is the major cause of the difference between the entire MC system and water as depicted in Fig. 4b. This process continues with higher temperature, with the formation of more and more hydrophobic aggregates [16]. As the temperature continues to increase, the three-dimensional network of MC chains is fully developed and it starts to take in water molecules and entrap them within the network cells. This leads to the reduction in entropy as some of water molecules become restrictive in the network cells. This reduction in the disorderliness of water molecules is balanced by the increase in disorderliness of the MC system, and thus we observed no decrease in dS/dT of the entire system as compared to that with water alone. Gradually, more and more water molecules become entrapped within the network, until all of them are held within the network cells, resulting in a fully developed and stabilized gel. As a result, the rise in dS/dT over the water-alone system reduces until it is no longer discernable. These observations were consistent for all MC concentrations as depicted in Fig. 5. With higher MC concentrations, the differences in dS/dT is higher between the entire system and that of water alone as expected.

Figures 4b and 5 also indicate that the entropy increase of the entire MC system correlates closely with that of free water around the offset temperature (towards the end of gelation). A study on the thermodynamic analysis of poly(2-hydroxyethyl) hydrogel by other researchers [20] revealed that the difference between the entropy change for water in gel and that of pure liquid water tends to be zero as water uptake by the gel network increases beyond 25%. This indicates that the behavior of sorbed water in gel do not differ significantly from that of free water in terms of entropy changes. This phenomenon may be explained by the presence of the different ‘states’ of water [21, 22] in the network due to the distance maintained by the water molecules from the polymer chains. The first water molecules which associate with the polymer chains in its immediate vicinity are considered as strongly bound water and thus they have the least mobility. Compared with the strongly bound water, other water molecules at a further distance from the chains have weaker bond with the polymer and thus possess more mobility and disorder. Thus, sorbed water at an even greater distance from the polymer chains can be considered as ‘free water’, which behaves in a manner similar to that of water-alone system. This implies that for the MC system, the entropy change for water in the gel network do not differ significantly from that for free water at and beyond the offset temperature. This explains the insignificant entropy increase observed towards the end of gelation.

For this hydrogel investigation, the degree of gelation α_g is a function of temperature only, unlike other polymerization processes such as the curing of thermosetting resins [23], the crystallization of thermoplastics [24] and the conversion of super-absorbing cross-linked hydrogels [25] where time is an additional important parameter. As such, α_g can be calculated using the DSC data either obtained experimentally or described using the C_p model as:

$$\alpha_g=\frac{\text{relative heat absorbed at any stage of gelation}}{\text{relative heat input required for complete gelation}}=\frac{\Delta H}{\Delta H_T} \tag{10}$$

where α_g describes the state of gelation which is directly linked to the thermodynamic conditions of the system. Thus, α_g=0 at T_{on} and α_g=1 when T=T_{off}. It is not necessary to add in the water effects for the degree of gelation calculations as only the relative variation

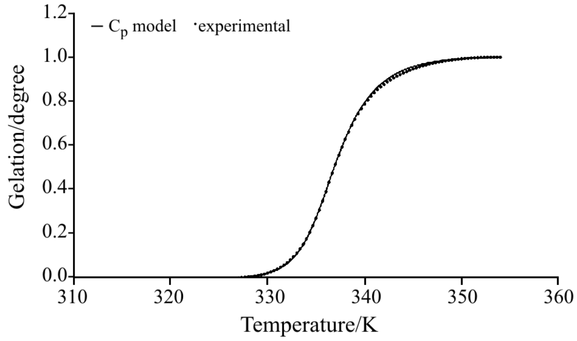

Fig. 6a Heating of 0.56 mass% MC

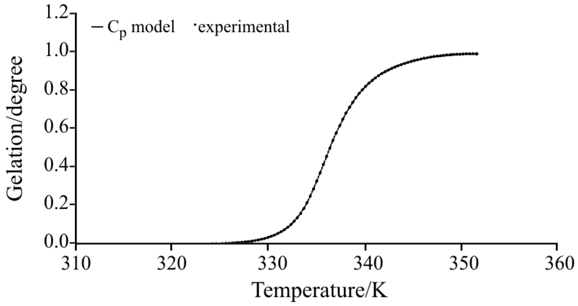

Fig. 6b Heating of 0.91 mass% MC

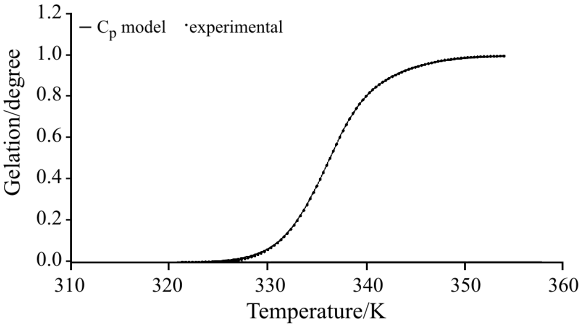

Fig. 6c Heating of 1.53 mass% MC

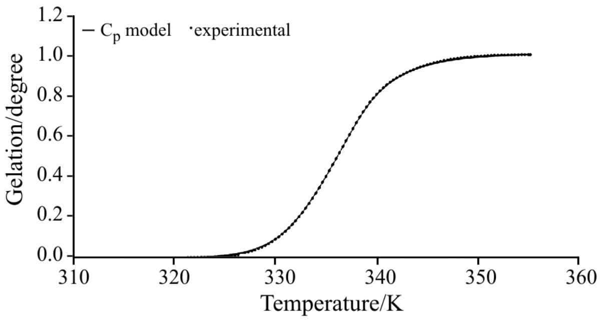

Fig. 6d Heating of 1.83 mass% MC

in C_p values are required for determining α_g. As the model could describe the variation of C_p well, it is therefore not surprising to find good agreement between the values of α_g obtained from the C_p model fitted directly to the experimental data in Fig. 6.

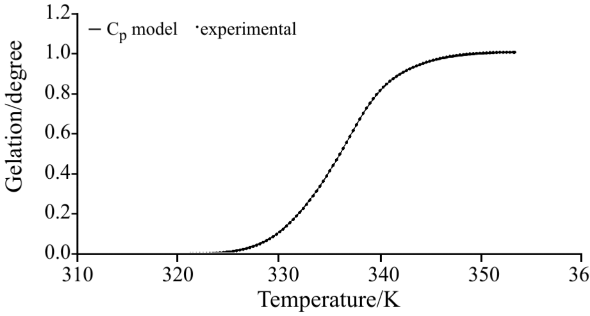

Fig. 6e Heating of 2.19 mass% MC

Conclusions

With an increase in MC concentration, gel formation involved more MC macromolecules, and an associated increase in enthalpy of the system. In addition, stronger gels were formed with an increase in MC concentration. The simulated heat capacity curves for the entire system (including that of water) represented the DSC data well and facilitated accurate calculation of thermodynamic parameters and variations in them. The variations in dS/dT followed a downward trend for all MC concentrations. Centered at around the peak temperatures, the increase in entropy (disorderliness) present in the entire MC system over of that of water alone was small, but significant. It indicates that this increase is caused dominantly by the MC system. Experimental data also indicated that δG is almost zero for all the samples at all the temperatures, i.e. the hydrogel systems attain and maintain equilibrium at isothermal conditions. This implies that the MC gel formation is a temperature-dependent process. Thus, a temperature change as well as an energy input is necessary to cause and to promote MC gelation.

Nomenclature

δG	Gibbs free energy change
δH	enthalpy change
δS	entropy change
ΔS	cumulative entropy change
ΔH	cumulative enthalpy change
ΔH_T	total enthalpy change
C_p	specific heat capacity
λ_i, C_i	empirical constants in C_p model
C_{pv1}, C_{pv2}	empirical constants in C_p model
T_{p1}, T_{p2}	empirical constants in C_p model
α_g	degree of gelation
$C_{p(max)}$	maximum heat capacity of DSC curve
$C_{p(avg)}$	average value of specific heat capacity over a temperature range
T_{on}	temperature (K) at which gelation begins
T_i	any given temperature (K)

T_p	temperature (K) at which C_p is maximum
T_{off}	temperature (K) at which gelation completes
T_{avg}	average temperature (K)

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