Influence of Surfactant Properties on Thermal Behavior and Sol–Gel Transitions in Surfactant-HPMC Mixtures

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ABSTRACT: Four surfactants, namely, sodium *n*-decyl sulfate (SDeS), sodium *n*-hexadecyl sulfate (SHS), sodium *n*-dodecyl sulfate (SDS), and Triton X-100, were used as additives to study thermal behavior and sol–gel transformations in dilute aqueous hydroxypropyl methyl cellulose (HPMC)/surfactant mixtures using micro-differential scanning calorimetry. The influence of anionic surfactant, SDS on the gelation varied with SDS concentration where the sol–gel transition started at a higher temperature. Shape of the thermograms changed from single mode to dual mode at the SDS concentration of 6 mM and higher. SDeS and SHS, however, resulted in "salt-in" effect of a different magnitude during gelation. Triton X-100, being a non-ionic surfactant, showed a minor "salt-out" effect on the thermo-gelation process. On the basis of different thermal behavior of anionic and non-ionic surfactant/HPMC systems, a mechanism is proposed explaining how the chemical structure and electro-charge of the surfactants affect the polymer/surfactant binding and polymer/polymer aggregation because of hydrophobic interaction during the sol–gel transition. © 2009 Wiley Periodicals, Inc. Journal of Applied Polymer Science 113: 2887–2893, 2009

Key words: HPMC; surfactant; calorimetry; gelation

INTRODUCTION

Amphiphilic nature of surfactants grants them special properties to introduce interactions with water-soluble polymers, especially those with hydrophobic segments/blocks. As far as ionic surfactants are concerned, reduction in surface tension and electrostatic interaction are the two main driving forces that induce variance of aggregation patterns and phase change in water-soluble polymers in aqueous media.[1,2]

Because of a range of applications in pharmaceuticals, cosmetics, and food industry,[3,4] behavior of aqueous mixtures of cellulose derivatives and surfactants has generated considerable interest among research community. Strong tendency of a surfactant to self-aggregation induces changes in the thermal behavior of cellulose derivatives during the sol–gel transformation process.[3–5] With priority binding to hydrophobic side chains of a polymer in an entropy-driven process, surfactant molecules tend to aggregate easily around such hydrophobic segments of the polymer in an aqueous environment. This promotes integration between the polymer chains and/or causes solubilization of the amphiphilic polymer to certain extent during the process.[5–7]

Hoffmann et al. investigated the effect of anionic surfactants such as sodium dodecylsulfate (SDS) and sodium tetradecylsulfate (STS) on the gelation of hydroxyethyl cellulose (HEC) and modified HEC samples with cationic groups (cat-HEC) or with a cationic and hydrophobic group (cat-HMHEC).[8] Kastner et al. reported that on the addition of an oppositely charged surfactant, modified HEC solutions showed an associative phase separation at certain concentration of the surfactant followed by re-solubilization with excess surfactant concentrations.[9] The cationic and hydrophobic parts of the modified HEC interacting synergistically with anionic surfactant molecules led to better viscoelastic properties than that of cationic HEC under the same conditions. According to Evertsson and Nilsson,[3] hydrophobically modified ethyl hydroxyethyl cellulose (HM-EHEC) self-associates and forms polymeric micelles in semi-dilute solutions. Significant rise in the micro-viscosity and reduction in the micropolarity were observed upon successive addition of SDS.[3] Minor non-cooperative SDS binding to HM-EHEC started at low concentration of SDS (<5 mM) followed by a highly cooperative binding region at SDS concentration of ≥5 mM. In general, monomeric surfactants and the composition of the formed micellar aggregation between the bound surfactant and the hydrophobic segments induce alignment of polymer chains as physical cross-link sites.[10]

The propensity of oppositely charged surfactants and polyelectrolytes (polymers) to bind together is governed by the critical aggregation concentration

(CAC). Thus, CAC relates to the concentration of the aggregation of surfactant and polymers together. The strong surfactant/polyelectrolyte interaction may lower the CAC value and counteract solubility of both components resulting in formation of gel because of associative phase separation.[11,12] In the case of surfactant/non-ionic polymer mixtures, significant interactions occur only after the surfactant concentration reaches its CAC value,[5] whereas the free surfactant molecules continue to bind to the polymer through adsorption or cluster formation until the state of saturation is reached. It is supposed that the non-ionic polymer will change into a polyelectrolyte-like polymer when ionic surfactant molecules are adsorbed onto the polymer via its hydrophobic tail. The electrostatic repulsions between ionic heads of the surfactant molecules result in conformational changes of the polymer chains and the microstructure of the corresponding gel.[13–16] As far as the ionic surfactants are concerned, anionic surfactants generally cause viscosity to increase in comparison with cationic surfactants because of stronger synergic interactions in a polymer/surfactant mixture; and the effect varies with different chain length in a homologous series of surfactants.[17,18]

Hydroxypropyl methylcellulose (HPMC) being a widely used cellulose-based polymer, its interaction with various surfactants has been of research focus. In this article, the effects of three anionic surfactants; namely, sodium *n*-dodecyl sulfate (SDS), sodium *n*-decyl sulfate (SDeS), sodium *n*-hexadecyl sulfate (SHS), and one non-ionic surfactant, Triton X-100, on thermal behavior of HPMC hydrogels are investigated. The purpose of the study is to determine effects of chemical structure and electrostatic properties of these surfactants, on the sol–gel transition behavior of HPMC during heating. The possible mechanisms that affect the sol–gel transitions in HPMC/surfactant systems are proposed through the variations in the chemical structure, molecular binding and the surface-active properties of the surfactants. Explanations are provided based on the different modes of molecular interaction in polymer–surfactant binding and polymer–polymer hydrophobic association. Discussions are related to the energy input to the polymer/surfactant systems. This work is expected help in accurately proposing a type and quantifying the addition of a surfactant to HPMC to suit an application. It will also highlight the specific energy requirements for gelation of surfactant-HPMC mixtures.

EXPERIMENTAL STUDIES

Materials

The HPMC $\{[C_6H_7O_2(OH)_{3-x-y}(OCH_3)_x(OCH_2CHOH-CH_3)_y]n\}$ used in this work was purchased from

Sigma-Aldrich (USA). Its molecular weight (M_n) was 86,000 and its 2-wt % aqueous solution has the viscosity of 4000 mPa s at 20°C. The average degrees of substitution (x) and (y) of methyl (CH_3) and hydroxypropyl (C_3H_7O) groups were 1.8–2.0 and 0.2, respectively. The HPMC was dried overnight at 60°C in vacuum and stored in a desiccator before use. SDS ($C_{12}H_{25}NaSO_4$), SDeS ($C_{10}H_{21}NaSO_4$), and Triton X-100 ($C_{34}H_{62}O_{11}$ for $x = 10$) were purchased from Sigma-Aldrich. SHS ($C_{16}H_{33}NaSO_4$) was ordered from Alfa Aesar, a Johnson Matthey Company (USA). The de-ionized (DI) water was obtained using Alpha-Q Millipore (Bedford, MA) water purification system.

Sample preparation

An aqueous solution of 1.00 wt % HPMC was prepared by dispersing appropriately weighed HPMC powder into DI water under stirring. The formed mixture was stored in a refrigerator (4°C) for 24 h until a homogeneous and transparent solution was obtained. Various surfactants were added in predetermined concentrations into the HPMC solutions and the mixes were stirred overnight. All the samples were stored in the refrigerator before any measurements.

Micro level thermal measurements

A differential scanning calorimeter (VP-DSC MC-2 microcalorimeter, MicroCal, USA) was used to study the thermal behavior of the HPMC/surfactant solutions. The procedure included heating the sample from 20 to 100°C and then cooling back to 20°C, both at the scanning rate of 1°C/min. DI water was used as the reference for all measurements. Before each test, the sample and reference cells (each having 0.516 mL capacity) were thoroughly cleaned and the instrument was calibrated. The relative heat capacity (C_p) was recorded during upscan (or the heating segment) after giving due consideration to the volume of the samples used. As a normal practice, DSC results were obtained after subtracting the results for the reference fluid, the DI water.

RESULTS AND DISCUSSION

It is generally regarded that changes in C_p with temperature (T) could be used to describe the thermogelation process or the sol–gel transitions for cellulose-based systems.[19] The onset and offset gelation temperatures correspond to the starting point of rising and the end point of diminishing C_p-T curves, commonly known as thermograms, observed during DSC measurements.
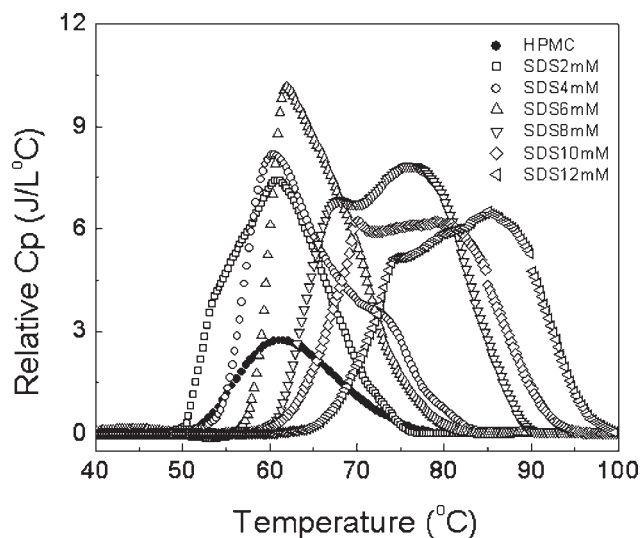
Figure 1 Relative heat capacity as a function of temperature for 1 wt % HPMC solutions with different concentrations of SDS.

Effect of SDS

The thermograms of HPMC/SDS solutions with different SDS concentrations recorded by micro-DSC during heating process are shown in Figure 1. Without SDS, the thermogram of the HPMC solution showed a low peak with its temperature at 61°C. With the addition of SDS, the area under the curve (or the enthalpy) and the position of the maximum or peak C_p changed. At the SDS concentrations of 2 and 4 mM, the peaks of the thermogram shifted slightly to lower temperatures. It may be said that the addition of SDS in such low concentrations had a slight "salt-out" effect on gelation of HPMC. The C_p values and the enthalpy for the SDS/HPMC solutions, however, increased significantly as compared to the pure HPMC solution. Other researchers also observed a similar phenomenon for a SDS/MC system.[20] In the case of 4 mM SDS/HPMC solution, the curve also registered a higher offset temperature. With SDS concentration of 6 mM, not only the peak of the corresponding DSC curve appeared at slightly higher temperature when compared with the pure HPMC solution, but also the onset of the sol–gel transition delayed and occurred at a higher temperature. The thermogram stood out with its peak much higher than the other SDS/HPMC mixtures. This shows that the SDS concentration of 6 mM had a significant and peculiar influence on the gelation of HPMC. At the SDS concentration higher than 6 mM, the sol–gel transition started at even higher temperatures. Although, the shape of the thermograms changed from single mode to dual mode with the addition of SDS, the change was very distinct for SDS concentrations of 8 mM and above. Each of the 8, 10, and 12 mM thermograms spread over a

broader temperature range, but with a reduced height of the peaks. Such drastic change in the gelation process for HPMC above the SDS concentration of 6 mM gave the indication that 6 mM be considered as the CAC value in the presence of HPMC.

By drawing logical inferences from the DSC observations made and taking some clues from the previous work of our group,[19] schematic diagrams as in Figure 2 illustrating interaction between HPMC and SDS as well as the gelation of HPMC/SDS system are constructed. Figure 2(a) shows solubilized HPMC because of the formed water cages around the hydrophobic side chains. This is an entropy-driven process and occurs at low energy levels. As discussed earlier, the presence of SDS in low concentrations have minor effect on the gelation temperature for HPMC. The entire gelation process occurs almost in a similar manner as for HPMC without any additives. First, the
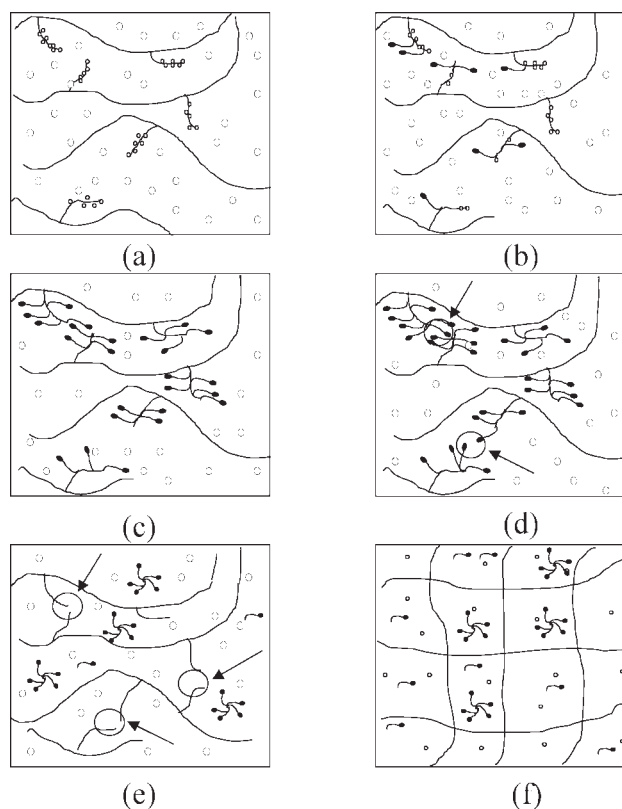
Figure 2 Schematic diagrams showing molecular interaction between HPMC and SDS: (a) HPMC with bound water cages; (b) HPMC with partially displaced water cages by the attached SDS molecules at the concentration below 6 mM; (c) HPMC saturated with SDS at its concentration between 6 and 8 mM; (d) induced aligning of HPMC with SDS concentration higher than 8 mM; (e) induced aggregation of hydrophobic parts of HPMC at the elevated temperature; and, (f) the final network structure of HPMC gel. (●⌒ represents polar head and hydrophobic tail of a surfactant molecule. Hollow circles represent water molecule and the long continuous lines depict HPMC molecules).
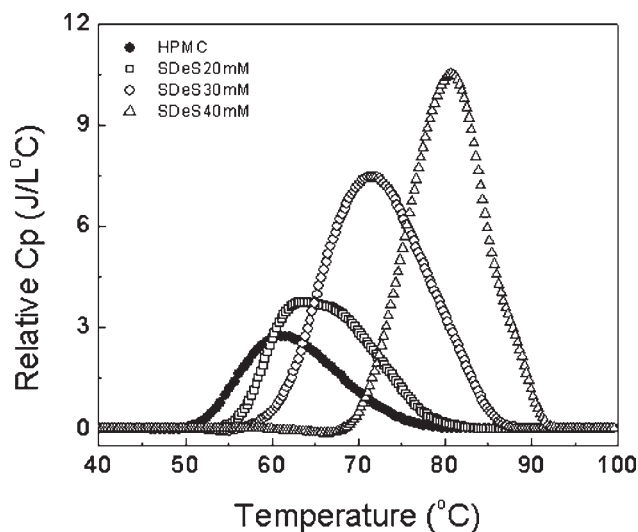
Figure 3 Relative heat capacity as a function of temperature for 1 wt % HPMC solutions with different concentrations of SDeS.

water cages are broken upon heating and the hydrophobic association of HPMC chains leads to a systemic aggregation bringing about the sol–gel transition.[21] The only difference is the increase in a transition energy at 2 and 4 mM SDS. Below 6 mM concentration, SDS molecules exist mostly as monomers. Some of the SDS molecules bind to the hydrophobic segments of the HPMC chains and eventually displace part of the bound water surrounding the corresponding hydrophobic segments of HPMC; refer Figure 2(b). Although the energy requirement for breaking the water cages before any gel formation starts, is reduced, higher energy and longer time are required to dismantle the bound surfactant molecules off the hydrophobic segments of the HPMC chains to cause proper gel formation. Thus, the relative heat capacity of the SDS/HPMC mixtures and the corresponding offset temperatures increased quantitatively in the presence of SDS.

When the SDS concentration is at its CAC value of 6 mM, binding of SDS to hydrophobic segments of HPMC occurs either through adsorption or through cluster formation until saturation because the formation of SDS/HPMC complex is energetically more favorable than the formation of SDS micelles. The critical micellization concentration (CMC) of SDS is $\sim$ 8 mM for a binary SDS/water system.[20] For SDS content between CAC (6 mM) and CMC (8 mM), surfactant molecules continually bind to the available hydrophobic sites of HPMC as either monomeric surfactants or partial micelle-like aggregations [Fig. 2(c)]. At the SDS concentration above 8 mM, a large amount of SDS molecules in the solution induce intermolecular aggregation of HPMC after binding themselves to the hydrophobic sites on the polymer chains as depicted in Figure 2(d). Such binding occurs at a temperature lower than the onset gelation temperature and continues until the saturation of the HPMC molecules with SDS; this was verified by other researchers through the measurement of the conductivity of similar system.[5] With temperature increasing further, the hydrophobic association between neighboring HPMC chains progresses until it reaches the saturation state inducing partial formation of the gel network. However, the entire process results in "salt-in" effect above 8 mM concentration of SDS. The first endothermic peak in the thermograms therefore appears at a higher temperature. With the temperature rising further, these bound surfactant and water cages get detached from the hydrophobic parts of HPMC exposing them to water. Consequently, intermolecular association between HPMC molecules starts to occur through physical association of hydrophobic groups [Fig. 2(e)]. At this stage, there are still some formation of SDS micelles float around. As the formation of gel network progresses, mobile species like the SDS micelles, the dismantled surfactant molecules, and water molecules, begin to get trapped within the formed cell-like structure of the gel [Fig. 2(f)]. This gel formation process attributes to the second peak in the thermograms. In the end, all surfactant and water get imbibed into the gel network, which develops into a well-stabilized entity at the offset temperature.
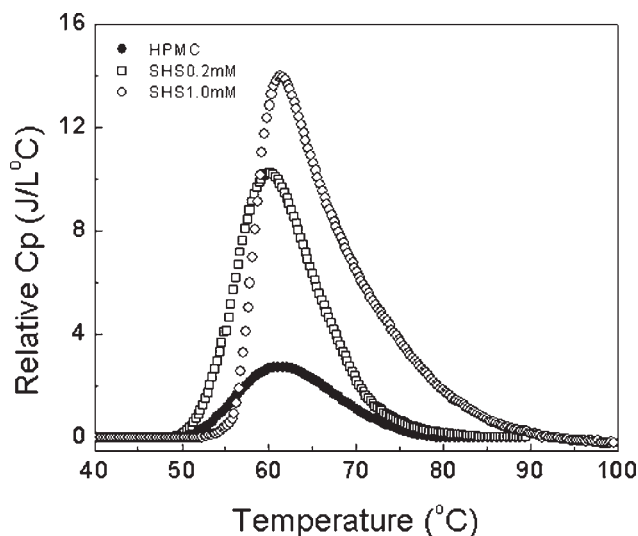
Effect of SDeS

Figure 3 shows the thermograms for HPMC with SDeS added in. It is reported that the CMC value for SDeS in aqueous solution is 33 mM.[22] Because the objective was to study and compare behaviors of surfactants at concentrations below and above CMC, SDeS was used in three concentrations, 20, 30, and 40 mM.

With the addition of SDeS at these three concentrations, i.e. 20, 30, and 40 mM, a strong "salt-in" effect was observed in the thermograms and the gelation of HPMC/SDeS mix occurred at higher temperatures. As shown in Table I, the occurrence of the

TABLE I
Temperature at Highest Relative $C_p(C_{p\text{-Peak}})$ with Various Surfactant Concentrations

	Surfactant concentration (mM)	Temperature at $C_{p\text{-Peak}}$ (°C)
HPMC	–	61.8
HPMC+SDeS	20	62.3
	30	71.0
	40	81.3
HPMC+SHS	0.2	61.3
	1.0	63.1
HPMC+Triton	0.1	61.0
	0.2	60.8
	1.0	60.0

Figure 4 Relative heat capacity as a function of temperature for 1 wt % HPMC solutions with different concentrations of SHS.

$C_{p\text{-peak}}$ on the thermogram shifted to a temperature 20°C higher than for the surfactant-free solution. Although the shape of the thermograms had only one peak, the temperature range for the sol–gel transition became narrower with the increase in the concentration of SDeS. Like SDS, SDeS, having a polar head and hydrophobic tail, has propensity to bind to the hydrophobic segments of HPMC. In the current study, because of its higher CMC concentration, the bound SDeS granted high-density electrostatic interactions of repulsive nature allowing more surfactant shells around the HPMC resulting in the higher onset gelation temperature as additional energy input was essential to break these shells.

Effect of SHS

The thermograms of HPMC in the presence of SHS are presented in Figure 4. With the addition of 0.2 mM SHS, the onset temperature for the HPMC solution did not change. The peak of the thermogram appeared at a temperature slightly lower than that for the pure HPMC solution, and a higher C_p was registered. It should be noted that SHS concentration of 0.2 mM is lower than its CMC, which is at 0.45 mM of SHS in aqueous solutions.[22,23] Thus, the addition of SHS had the similar influence as that of SDS at low concentrations. With the increase in SHS concentration from 0.2 mM to 1.0 mM, gelation of the HPMC solution started at a higher temperature, the behavior similar to for SDeS/HPMC mixtures. The corresponding thermogram shifted slightly to the right side although the peak of the thermogram appeared nearly at the same temperature for the SHS-free HPMC solution.

It may be noted that dual peaks were found at the SDS concentrations above its CAC. However, only single peaks were observed for SDeS and SHS at their respective concentrations above CAC. This is primarily because of the different hydrophobic alkyl chains and aggregation properties of these three surfactants, which also leads to different activation energies. The difference on the alkyl chain plays a great role in causing variance of CAC and/or CMC, which indicates that the aggregation of surfactants and polymers is influenced by the chemical structure of the surfactants.

Effect of triton

The ionic surfactant induce strong electrostatic interactions when introduced in neutral polymers while interactions between non-ionic surfactants and neutral polymers are very weak.[24,25] Hydrophobic association and hydrogen bonding thereof are the main interactions involved in the aggregation/dismantling of polymer/non-ionic surfactant systems.[26] As seen in Figure 5, when Triton X-100 was introduced into the aqueous solutions of HPMC, the gelation patterns exhibited a different trend when compared with those observed for anionic surfactants (SDS, SHS, and SDeS). With the addition of Triton in different concentrations, i.e. 0.1, 0.2 and 1.0 mM, a minor "salt-out" effect (about 1.8°C as reported in Table I) was observed and the HPMC gelation occurred at lower temperatures. The enthalpy change in the gelation process was much less when compared with the anionic surfactants. It is reported that the CMC value for Triton X-100 in aqueous solution is $\sim$ 0.2 mM.[27] At the Triton X-100 concentration up to its CMC, the enthalpy increase during sol–gel transition was not significant. Above CMC,
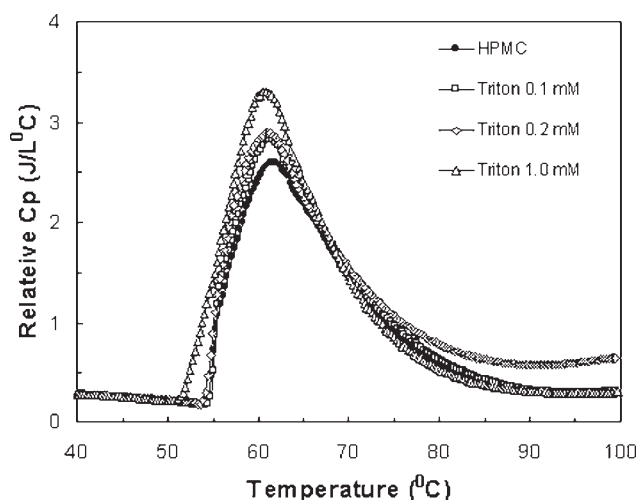
Figure 5 Relative heat capacity as a function of temperature for 1 wt % HPMC solutions with different concentrations of Triton.

relatively higher C_p ($C_{p\text{-peak}}$) was noticed. However, shape of the thermogram was very similar to that for the surfactant-free HPMC solution. This essentially points out to the weak interaction between the surfactant and the polymer. In addition, this may be attributed to the absence of any dominating electrostatic interaction, as Triton X-100 molecules have no polar head.
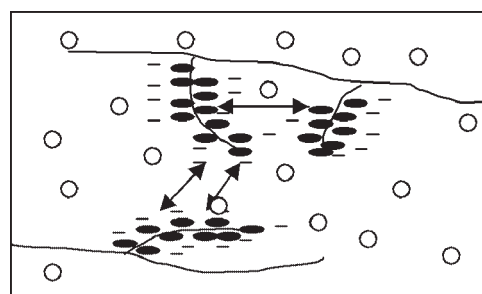
Electrostatic effect

As seen in Figure 2(b) for SDS, some of the fully integrated water cages get broken partially when some SDS molecules get attached to the hydrophobic segments of HPMC. As a result, such partially "caged" hydrophobic segments of HPMC show some polarity because of the polar heads of the attached SDS molecules. The electrostatic repulsion of the bound SDS hinders the movement of the approaching HPMC chains in the neighborhood. As such, more energy is then required to overcome these phenomena and dismantle the surfactant/polymer aggregation.

The different strengths of electrostatic repulsion for SDeS and SHS molecules, as shown schematically in Figure 6(a,b), seemed to be the key factor in determining the behavioral differences during the thermally driven sol–gel transitions in HPMC-surfactant mixtures. The strength of the electrostatic repulsion and its variation for SDeS and SHS (it is much higher for SDeS) affect the processes of inducing micelle like aggregation and dismantling of the bound surfactant. This, in turn, influences the gelation, decides the thermogram pattern, and determines the overall enthalpy for the sol–gel transition.

Considering its non-ionic nature, the addition of Triton X-100 did not introduce any electro-statically repulsive interactions among the surfactant molecules [Fig. 6(c)] at the time when the hydrophobic segments of HPMC were coming closer. Consequently, energy required for dismantling any aggregation of the surfactant molecules was much less, which was also due to the lower CMC of Triton X-100.

Increased energy requirement

With the addition of either anionic or non-ionic surfactant, the bound surfactant around the hydrophobic parts of HPMC requires more energy to induce alignment of the polymer chains and dismantle the micellar structure. This automatically raises the energy requirement for the system. The magnitude of it, is however controlled by two phenomena: one, the intensity of the aggregation of surfactant molecules at the hydrophobic parts of the polymer, and two, the strength of the electrostatic repulsion produced by the surfactant. Both these phenomena were weakly pres-

(a)
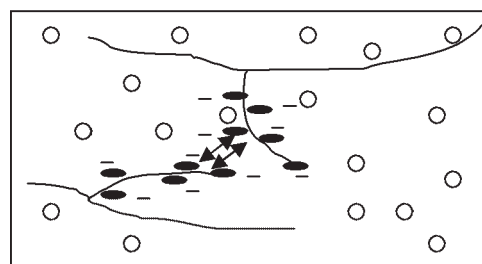
(b)
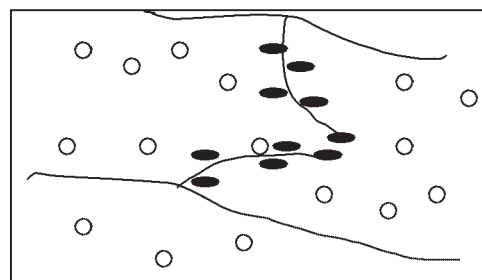
(c)

Figure 6 Interaction between surfactant-bound HPMC molecules: (a) SDeS; (b) SHS; (c) Triton. (⬬ represents polar head of surfactant molecule and, ↔ represents electro-static repulsion.).

ent for Triton X-100 and therefore, only a slight increase in the peak C_p and the enthalpy were seen. In contrast, anionic surfactants raised the energy requirements for the HPMC gelation.

CONCLUSIONS

This study demonstrated that the thermal behavior of HPMC hydrogels is affected by addition of surfactants. The effect, however, varied for anionic (SDS, SDeS, SHS) and non-ionic (Triton X-100) surfactants. Anionic surfactants increased the energy barrier of the sol–gel transition because of their priority binding to the hydrophobic parts of HPMC inducing polar outshells, which hinder the free access to HPMC chains at elevated temperature. The non-ionic

surfactant showed much less influence on the gelation of HPMC solution. Difference in the chemical structure and electrostatic interaction between the surfactant and HPMC molecules determined the thermal energy requirements for sol–gel transitions in the ternary mixtures of surfactant/HPMC/water.

References

1. Piculell, L.; Thuresson, K.; Lindman, B. Polym Adv Technol 2001, 12, 44.
2. Zhao, G. Q.; Chen, S. B. Langmuir 2007, 2, 9967.
3. Evertsson, H.; Nilsson, S. Carbohydr Polym 1999, 40, 293.
4. Kjoniksen, A. L.; Knudsen, K. D.; Nystrom, B. Eur Polym J 2005, 41, 1954.
5. Sovilj, V. J.; Petrovic, L. B. Carbohydr Polym 2006, 64, 41.
6. Piculell, L.; Lindman, B. Adv Colloid Interface Sci 1992, 41, 149.
7. Su, J. C.; Liu, S. Q.; Joshi, S. C.; Lam, Y. C. J Appl Polym Sci 2008, 93, 495.
8. Hoffmann, H.; Kastner, U.; Donges, R.; Ehrler, R. Polym Gels Networks 1996, 4, 509.
9. Kastner, U.; Hoffmann, H.; Donges, R.; Ehrler, R. Colloids and Surf A: Physicochem Eng Aspects 1996, 112, 209.
10. Piculell, L.; Thuresson, K.; Ericsson, O. Faraday Discuss 1995, 101, 307.
11. Lapitsky, Y.; Kaler, E. W. Coll Surf A 2004, 250, 179.
12. Lapitsky, Y.; Kaler, E. W. Coll Surf A 2006, 282, 118.
13. Bystrom, B.; Roots, J.; Carlsson, A.; Lindman, B. Polymer 1992, 33, 2875.
14. Nilsson, S.; Thuresson, K.; Hansson, P.; Lindman, B. J Phys Chem B 1998, 102, 7099.
15. Patruyo, L. G.; Muller, A. J.; Saez, A. E. Polymer 2002, 43, 6481.
16. Piculell, L.; Egermayer, M.; Sjostrom, J. Langmuir 2003, 19, 3643.
17. Tanaka, R.; Meadows, J.; Williams, P. A.; Phillips, G. O. Macromolecules 1992, 25, 1304.
18. Thuresson, K.; Lindman, B.; Nystrom, B. J Phys Chem B 1997, 101, 6450.
19. Joshi, S. C.; Lam, Y. C. J Appl Polym Sci 2006, 101, 1620.
20. Wang, Q.; Li, L.; Liu, E. J.; Xu, Y. R.; Liu, J. H. Polymer 2006, 47, 1372.
21. Liu, S. Q.; Joshi, S. C.; Lam, Y. C.; Tam, K. C. Carbohydr Polym 2008, 72, 133.
22. Anlansson, E. A. G.; Wall, S. N.; Almgren, M.; Hoffmann, H.; Klelmann, I.; Ulbrlcht, W.; Zana, R.; Lang, L.; Tondre, C. J Phys Chem 1976, 80, 905.
23. Holmberg, K.; Jönsson, B.; Kronberg, B.; Lindman, B. Surfactants and Polymers in Aqueous Solution, 2nd ed.; John Willey & Sons: Chichester, England, 2003.
24. Winnik, F. M.; Regismond, S. T. A. Colloids Surf A 1996, 118, 1.
25. Thuresson, K.; Lindman, B.; Nystrom, B. J Phys Chem B 1997, 01, 6450.
26. Anghel, D. F.; Winnik, F. M.; Galatanu, N. Colloids Surf A 1999, 149, 339.
27. Yeom, I. T.; Ghosh, M. M.; Cox, C. D.; Robinson, K. G. Environ Sci Technol 1995, 29, 3015.