Carbohydrate Polymers 51 (2003) 57–61

Carbohydrate Polymers

www.elsevier.com/locate/carbpol

Effect of alcoholic, glycolic, and polyester resin additives on the gelation of dilute solution (1%) of methylcellulose

P.P. Kundu[a,*,1], M. Kundu[b], M. Sinha[a], S. Choe[c], D. Chattopadhayay[d]

[a]*Department of Chemical Technology, Sant Longowal Institute of Engineering and Technology, Longowal 148106, Punjab, India*
[b]*Quarter No. IV/81, SLIET Campus, Longowal 148106, Punjab, India*
[c]*Department of Chemical Engineering, Inha University, Inchon 402751, South Korea*
[d]*Department of Material Engineering, SBSCET, Ferozepur, Punjab, India*

Received 27 November 2001; revised 17 April 2002; accepted 18 April 2002

Abstract

The effect of various additives, such as alcohols, glycols, and polyester resins on the gel temperature of dilute solutions (1% by weight) of methylcellulose (MC) has been studied. The gel temperatures of 1% MC solution with all the used additives except polyvinyl alcohol (PVA) were higher than that of the pure 1% MC solution, which is 50 °C. The gel temperature increased with r (r is a ratio of wt% of additives to that of MC), reached a maxima followed by a decrease for succinic, octane dioic, azeilic, and pimelic acid based polyester. In addition to this variation pattern in gel temperature, phase separation succeeded at higher r values on the addition of polyvinyl and benzyl alcohol, ethanol, propanol, butyl cellosolve, and polyethylene glycol. But for ethylene, diethylene and tetraethylene glycols, the gel temperature continuously increased with r, followed by the phase separation. The increase in gel temperature induced by the used additives except PVA is suggested to be the effect of the predominance of pseudo-surfactancy over co-solvency. © 2003 Elsevier Science Ltd. All rights reserved.

Keywords: Gel temperature; Alcoholic and glycolic additives; Co-solvency; Pseudo-surfactant; 1% solution of methylcellulose

---

1. Introduction

Long back, it was reported (Heymann, 1935) that aqueous solutions of methylcellulose (MC) form gel upon heating. These gels are completely reversible in that they are formed upon heating and liquefy upon cooling (Sarkar, 1979). Thermally reversible gelation of aqueous solutions of macromolecules has been identified as the formation of a three-dimensional cross-linked network structure (Heymann, 1935). Since the sol–gel transformation is reversible within a narrow temperature range, it does not involve the making or breaking of any covalent bonds. The quasi-cross-linkage in gel network is due to secondary valance force as the solvating power of the medium decreases. Most macromolecules in solutions exist as randomly coiled isolated chains. When the temperature is decreased or increased beyond the gel temperature at appreciable concentration, the polymer begins to reconstitute the original solid-state structure. Commercial MC is a heterogeneous polymer consisting of highly substituted hydrophobic zones and less substituted hydrophilic zones. Gelation is therefore an intermediate non-equilibrium metastable state in which a three-dimensional network structure is formed due to secondary valence forces. The major discussions concern the nature of the zones responsible for gelation (Hirrien, Chevillard, Desbrieres, Axelos, & Rinaudo, 1998). MC undergoes thermoreversible sol–gel transformation, when an extremely dilute (Kundu & Kundu, 2001), semi-dilute (Sarkar & Walker, 1995) or moderately concentrated (Arisz, Hendrikus, & Jaap, 1995; Heymann, 1935) solution of MC is heated. The precipitation temperature, gelation temperature, and gel strength of MC solution were determined as functions of molecular weight, degree of methyl substitution, concentration of solution and presence of additives (Kundu & Kundu, 2001; Sarkar, 1979). It is reported earlier that the sol–gel transformation temperature, known as gel temperature, is sufficiently altered by adding some extraneous materials. These foreign materials may be diluents or co-solvents of water, such as ethanol (Sarkar, 1979) co-solute of MC like salts or urea (Bardhan, Mukhopadhyay, & Chatterjee, 1977; Sarkar, 1979). It is reported elsewhere (Cabane, Lindell, Engstrom, & Lindmann, 1996; Kundu & Kundu, 2001; Nystrom &

---

[*] Corresponding author.
E-mail address: ppk923@yahoo.com (P.P. Kundu).
[1] Presently on leave to Inha University, South Korea.

0144-8617/03/$ - see front matter © 2003 Elsevier Science Ltd. All rights reserved.
PII: S0144-8617(02)00107-8

Lindmann, 1995; Wang, Lindwell, & Olofsson, 1997) that the gel temperature of cellulose ethers depends on r (a ratio of wt% of additives to that of MC).

We have previously reported the effect of salts, surfactant and their doses on the gelation of extremely dilute solutions (below 1%) of MC (Kundu & Kundu, 2001). It was concluded that the addition of salts in dilute MC solution lowers the gel temperature of MC due to its dehydration effect and the gelation process depends on r (a ratio of wt% of additive to that of MC) (Kundu & Kundu, 2001).

Till now, the reported literature mainly concentrates on the effect of well known ionic surfactants, such as sodium lauryl sulphate (SLS; Kundu & Kundu, 2001) and sodium dodecyl sulphate (SDS; Nystrom & Lindmann, 1995; Wang et al., 1997) to the gel temperature of MC. On the other hand, it was mentioned (Sarkar, 1979) that the gel temperature of MC could be altered by the hydroxyl containing additives; some can elevate (in case of ethanol and propylene glycol (PG)) due to their action as solubilizers or reduce (in case of sucrose and glycerol) due to their electrolyte action. Reports are also available that long chain alcohols and glycols can act as non-ionic surfactants. Till date, there is no report about the effect of concentration, variation of chain lengths of these alcoholic and glycolic additives. In this article, the glycolic and alcoholic additives and their doses are varied at a fixed concentration of MC solution. Thus, the present report aims at understanding the effect of various additives (long or short), such as alcoholic, glycolic and polyesters (containing hydroxyl end groups) on the gelation of dilute solution (1%) of MC.

2. Experimental

2.1. Materials

MC, laboratory grade in powder form was supplied by SD Fine-Chem. Ltd, Biosar (India). Viscosity of 2% aqueous solution at 20 °C as supplied by the manufacturer is about 400 cP. The weight average molecular weight of MC is 1,30,000 and its polydispersity index is 1.8. The average degree of methyl substitution (DS) is 2.1. The DS in MC is very important as it was reported (Hirrien, Desbrieres, & Rinaudo, 1996) that MC agglomerates only above DS of 1.5. The aqueous solutions were prepared by dissolution of dried MC in demineralized water at 50 °C and the solution was kept at around 10 °C in a freezer for 24 h to assure a complete dissolution. The required amount of MC was dissolved to prepare solutions up to 1% concentrations without any aggregates at low temperature (Sarkar, 1979). Ethanol: laboratory grade bp 79 °C, supplied by Loba Chemie Pvt. Ltd, Bombay; propanol: laboratory grade bp 98 °C, supplied by Sisco Research Laboratory Pvt. Ltd, Bombay; butyl cellosolve (BC), $C_4H_9{-}O{-}CH_2{-}CH_2{-}OH$: laboratory grade bp 171 °C, supplied by C.D.H. Laboratory Reagent Pvt. Ltd, New Delhi (India); ethylene glycol, $HO{-}(CH_2)_2{-}OH$; diethylene glycol, $HO{-}(CH_2)_4{-}OH$; tetraethylene glycol, $HO{-}(CH_2)_8{-}OH$, laboratory grade supplied by E. Merck India Ltd, Bombay (India) and PG, $CH_3{-}CH(OH){-}CH_2{-}OH$, laboratory grade bp 188 °C was supplied by Ranbaxy Laboratory Pvt. Ltd, S.A.S. Nagar (India). Poly(vinyl alcohol), solid, laboratory grade; benzyl alcohol, liquid, laboratory grade; succinic acid, $HOOC{-}(CH_2)_2{-}COOH$, adipic acid, $HOOC{-}(CH_2)_4{-}COOH$: solid, laboratory grade, supplied by Loba Chemie Pvt. Ltd, Bombay; pimelic, $HOOC{-}(CH_2)_5{-}COOH$; octane dioic, $HOOC{-}(CH_2)_6{-}COOH$ and azeilic acid, $HOOC{-}(CH_2)_7{-}COOH$: solid, laboratory grade, supplied by E. Merck India Ltd, Bombay.

2.2. Synthesis of polyester resins

The reaction mixtures consisting of 1:1.1 molar ratios of diacids (succinic, adipic, pimelic, octane dioic, and azeilic acid) and PG along with small proportion of catalyst (dilute NaOH solution) were taken in a two-necked flask fitted with a reflux condenser in one neck (Ravve, 1995; Sandler & Karo, 1974). A U-tube, which contains a thermometer immersed in glycerol, was fitted in another neck. The reaction mixture was refluxed at 90 °C for 30 min and then water vapor was distilled off after neutralization with succinic acid for another 40–50 min. The polyester resin samples were collected after each 10 min during the distillation at low pressure (vacuum −10 kPa). Initially, the distillation temperature was around 110 °C. As the distillation process continued, the distillation temperature was rising with elapsed time and reached to a higher value of around 160 °C after 50 min. The increase in distillation temperature indicates the formation of polymers. The polymerization reaction is incomplete leading to low molecular weight (oligomeric) (Kundu, Raina, & Verma, 2002) aliphatic polyesters. If the distillation continues for more time, high vacuum is needed to control the polymerization reaction. For complete polymerization, along with high vacuum, an inert reaction atmosphere (N_2) is also required to avoid undesired oxidized side products (Ravve, 1995; Sandler & Karo, 1974). In the present study, although inert atmosphere was not maintained, but sufficiently low polymerization temperature hinders formation of side oxidized product. Still, there is a possibility of the presence of oxidized polyester in small proportion in some collected samples after long time distillation (40 min). The collected samples were added to distilled water for the precipitation of polyester and subsequent washing off the reactants including sodium carboxylate of the diacid formed during the intermediate phase of the reaction. The washed polyester was dried under vacuum at 70 °C for 24 h. All the polyester samples taken during distillation are soluble in warm water (40 °C) up to 0.5% of aqueous solution. The polyester resins formed from diacids and PPG were collected after 40 min of distillation

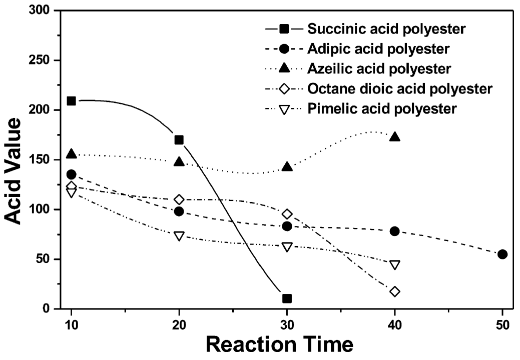

Fig. 1. Variation of acid value (mg of NaOH/g of polyester) with reaction time in minutes.

and added into the measured proportion to (1%) of MC solution. The resulting solutions were heated to study how the polyester additives affect on the gel temperature. The acid values in mg of NaOH/1 g of polyester sample were calculated from the titration of each polyester sample against dilute NaOH solution.

3. Results and discussion

Fig. 1 shows the variation of the acid values of polyester resins against reaction time. The reaction between diacids and PG proceeds towards the forward direction-giving rise to the polyester resin with distillation. Thus, the reaction time considered here is actually the distillation time. It is evident from Fig. 1 that the acid value decreases with time for all diacids except for azeilic acid based polyester, which shows increase after 30 min. The decrease in acid value with reaction time implies the formation of polyester resins, whereas the increase in acid value for azeilic acid polyester is an indication of its oxidation at the distillation temperature. On the other hand, adipic acid polyester shows slight decrease in acid value with reaction time indicating a prone to oxidation.

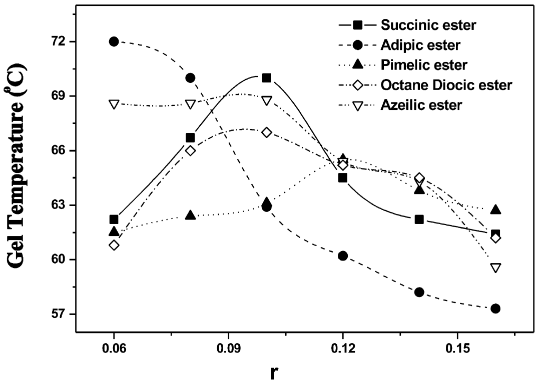

Fig. 2. Variation of gel temperature (°C) with r (ratio of wt% of polyester resin to that of MC, 1%) for succinic, adipic, pimelic, octane dioic, and azeilic acid ester of PG.

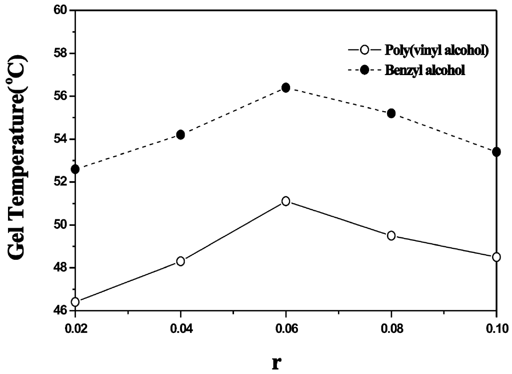

Fig. 3. Variation of gel temperature (°C) with r (a ratio of wt% of PVA and BA to that of 1% MC).

The variation of the gel temperature with r (a ratio of wt% of polyester resin to that of MC solution) for succinic, adipic, pimelic, octane dioic, and azeilic acid based polyester resin is shown in Fig. 2. Since the concentration of MC is kept constant at 1% by weight, the increase in r is an implication of an increase in polyester concentration. In addition, the gel temperature increases with r, reaches a maxima (at $r = 0.1$ for succinic, azeilic and octane dioic acid and at $r = 0.12$ for pimelic acid based polyester), then decreases. This type of variation in gel temperature was reported earlier in the systems, where surfactants were added to the MC solution (Kundu & Kundu, 2001; Nystrom & Lindmann, 1995; Sarkar, 1979; Wang et al., 1997). Thus, the variation of the gel temperature upon addition with these polyesters suggests that they act as surfactants. However, the above behavior was not observed for adipic acid based polyester, instead, the gel temperature keeps decreasing with r, due to the oxidation during its formation. The oxidized product (epoxy or carboxylic polyester) is acidic material, which is electrolytic in nature. It was mentioned (Sarkar, 1979) that the addition of electrolytes, such as salts decreased the gel temperature of the aqueous solution of non-electrolytic polymer solutions (e.g. MC solution). Thus, the oxidized product shows salting effect in gelation (like the pure diacids and salts). The salting effect caused by oxidation is opposing the surfactant effect of the polyester. In the case of adipic acid polyester, although the gel temperature decreased with r, it never reached to the value as low as that of the pure 1% MC solution, which is of 50 °C (Kundu & Kundu, 2001). This may be the indication of the predominance of surfactancy over salting.

The variation of the gel temperature against r (a ratio of wt% of polyvinyl alcohol (PVA) or BA to that of MC) for the fixed concentration of MC (1% by weight) is shown in Fig. 3. Since the concentration of MC is fixed, the variation of r means the variation of the concentration of the additives (PVA and BA). In this figure, the gel temperature increases with r, reaches a maxima at $r = 0.06$, then decreases. It is reported (Kundu & Kundu, 2001; Nystrom & Lindmann, 1995; Sarkar, 1979; Wang et al., 1997) that for ionic surfactant, the sol–gel transformation phenomenon appears in the limit of $0.02 < r < 0.1$, beyond which phase-separation occurs. From Fig. 3, it seems that both BA and

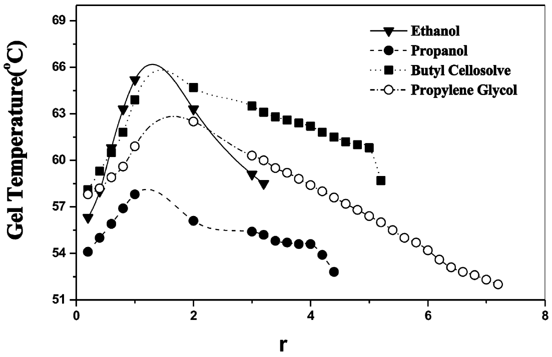

Fig. 4. Variation of gel temperature (°C) with *r* (a ratio of wt% of alcohols and glycols to that of 1% MC).

PVA behave like a non-ionic surfactant although PVA and BA are structurally different from the ionic salts of long chain fatty acids, such as SLS or SDS. The ionization of PVA and BA is not possible, but they may help in forming network of the MC necklaces leading to its gelation due to the presence of polar –OH group. Thus, PVA and BA are suggested to behave like a surfactant.

In addition, in Fig. 3, the gel temperature of BA is higher than that of PVA at the same *r*. Since the molecular weight of BA is much smaller than that of PVA, it can easily come in close vicinity of MC molecule (hydrophilic part) and solvates them. Thus, BA acts as a surfactant of MC molecules. The solvating strength and the unstrained positioning of BA molecules in the interstitial space during the formation of MC network seem to help its aggregation leading to gelation at much higher temperature.

We reported elsewhere (Kundu & Kundu, 2001) that 1% MC solution exhibited the gel temperature at 50 °C. But in Fig. 3, the gel temperature of 1% MC increases to a higher value on the addition of BA. This may be due to the role as co-solvent and pseudo-surfactant. On the other hand, incorporation of PVA to 1% MC solution leads them to compete each other during the dissolution in water. Thus, PVA acts as a co-solute of MC. In the case of PVA, its co-solute effect is dominant over pseudo-surfactancy inducing the decrease in gel temperature.

In Fig. 4, the variation of the gel temperature of 1% MC solution with various additives, such as ethanol, propanol, BC, and PG against *r* is plotted. It is evident from the plot that the gel temperature increases with *r* up to a maximum value at $r_{\max}$ ($r_{\max} = 1.2$, 1.3, 1.5 and 1.8 for propanol, ethanol, BC and PG, respectively). Beyond the maximum, the gel temperature decreases, then finally phase-separation occurs at $r = 3.5$, 4.5, 5.4 and 7.2, respectively. Since the molecular weights of alcoholic additives are small like water, they can homogeneously be mixed at molecular level with water in the whole range of compositions. Formation of fewer networks of MC aggregates by the pseudo-surfactant necklaces at low *r* is due to the solvating strength of MC favored by alcoholic additives. Alcoholic additives favor the formation of intermolecular hydrogen bonding between water and MC molecule. At low concentration of alcoholic additives, pseudo-surfactant effect is pronounced and this induces the increase in gel temperature. Alcoholic additives may act as pseudo-surfactant, as well as co-solvent of water. The co-solvency effect of alcoholic additives can disrupt the water–MC network, whereas pseudo-surfactant effect may help the formation of the network. At sufficiently high concentration, co-solvency effect is predominant leading to decrease in gel temperature. At extremely high concentration of alcoholic additives, the water–MC network may be destroyed due to its co-solvency effect.

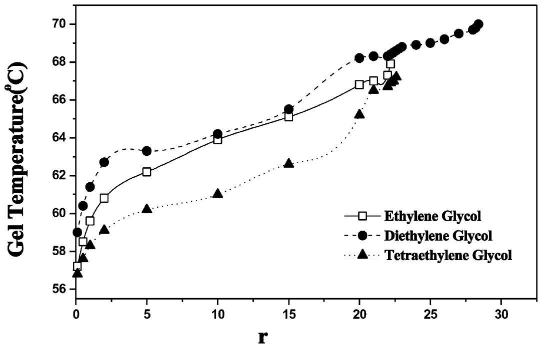

Fig. 5. Variation of gel temperature (°C) with *r* (ratio of wt% of glycols to that of MC, 1%) for ethylene, diethylene, and tetraethylene glycol.

Fig. 5 exhibits the variation of the gel temperature in the presence of ethylene, diethylene and tetraethylene glycols against *r* for the fixed concentration of MC (1%). The gel temperature augments dramatically up to $r < 2.5$, then continuously increases with *r* of up to the *r*-value at 22.2, 28.2 and 22.6 for ethylene, diethylene and tetraethylene glycol, respectively, and beyond that phase-separation occurs. These glycolic additives can act as pseudo-surfactant, as well as co-solvent. It was reported elsewhere (Wang et al., 1997) that the longer the chain length of hydrocarbon, the higher the pseudo-surfactant effect was observed. In our systems, DEG exhibited the highest gel temperature at a fixed value of *r*. This behavior may be explained by the easy fitment of DEG molecules into the interstitial spaces during network formation of MC molecules. On the other hand, TEG molecules seem to be strained during gelation of MC molecules due to their comparatively longer chain length. Thus, TEG exhibited the lowest gel temperature among three glycols. The increase in pseudo-surfactancy effect of these glycols with *r* enhances the aggregation between MC and water molecules through intermolecular hydrogen bonding.

4. Conclusion

In this article, the effect of various additives, such as alcoholic, glycolic materials and polyester resins on the gel temperature of dilute solutions (1% by weight) of MC has been studied. The additives used for this study are ethanol, propanol, PVA, BA, BC, PG, EG, DEG, TEG, and some polyester based on succinic, adipic, pimelic, azeilic and octane dioic acids and PG. The lowering in acid value with reaction time indicates the formation of polyester resin formed from some acids and PG. The gel temperatures of 1% MC solution with the used additives except PVA were higher than that of the pure 1% MC solution, which is 50 °C. The gel temperature increased with *r* (*r* is a ratio of wt% of additives to that of MC), reached a maximal at $r = 0.1$ for succinic, octane dioic and azeilic acid, and $r = 0.12$ for pimelic acid based polyester, and then decreased. In addition, the addition of PVA and BA induced an initial increase in the gel temperature of up to $r = 0.06$ followed by a decrease, then ultimately phase-separation occurred at $r > 0.1$. The variance of the gel temperature with *r* suggests that BA behave like a pseudo-surfactant and that PVA act as a co-solute. The gel temperature increases with *r*, reaches a maximum, followed by its decrease and then ultimately leads to phase separation at *r*-value of 3.5, 4.5, 5.4 and 7.2 for ethanol, propanol, BC and PG, respectively. Whereas for EG, DEG and TEG, the gel temperature continuously increased of up to the *r*-value of 22.2, 28.2 and 22.6, respectively, where the phase separation occurred. Thus, the increase in gel temperature with the additives except PVA is suggested to be the effect of the predominance of pseudo-surfactancy over co-solvency.

Acknowledgments

The corresponding author (PPK) is grateful to Dr R.C. Chauhan, Director, SLIET for his tireless encouragement to carry out this work.

References

Arisz, P. W., Hendrikus, J. J. K., & Jaap, J. B. (1995). Substituent distribution along the cellulose backbone in *O*-methylcelluloses using GC and FAB-MS for monomer and oligomer analysis. *Carbohydrate Research*, *271*, 1.

Bardhan, K., Mukhopadhayay, S., & Chatterjee, S. R. (1977). Grafting of acrylamide onto methylcellulose by persulphate ion. *Journal of Polymer Science: Polymer Chemistry*, *15*(1), 141.

Cabane, B., Lindell, K., Engstrom, S., & Lindmann, B. (1996). Microphase separation in polymer + surfactant systems. *Macromolecules*, *29*, 3188.

Heymann, E. (1935). Studies on sol–gel transformations. 1. The inverse sol–gel transformation of methylcellulose in water. *Transactions of the Faraday Society*, *31*, 846.

Hirrien, M., Desbrieres, J., & Rinaudo, M. (1996). Physical properties of methylcelluloses in relation with the conditions for cellulose modification. *Carbohydrate Polymers*, *31*, 243.

Hirrien, M., Chevillard, C., Desbrieres, J., Axelos, M. A. V., & Rinaudo, M. (1998). Thermogelation of methylcellulose: New evidence for understanding the gelation mechanism. *Polymer*, *39*, 6251.

Kundu, P. P., & Kundu, M. (2001). Effect of salts and surfactant and their doses on the gelation of extremely dilute solutions of methylcellulose. *Polymer*, *42*(5), 2015.

Kundu, P. P., Raina, K. K., & Verma, G. (2002). Influence of different polymers and their molecular weight on the textural and electro-optical behavior of polymer dispersed liquid crystals. *Journal of Applied Polymer Science*, in press.

Nystrom, B., & Lindmann, B. (1995). Dynamic and viscoelastic properties during the thermal gelation process of a nonionic cellulose ether dissolved in water in the presence of ionic surfactant. *Macromolecules*, *28*, 967.

Ravve, A. (1995). *Principles of polymer chemistry*. New York: Plenum Press. p. 287..

Sandler, S. R., & Karo, W. (1974) (*Vol. 1*). *Polymer synthesis*, New York: Academic Press. p. 61.

Sarkar, N. (1979). Thermal gelation properties of methyl and hydroxypropyl methyl cellulose. *Journal of Applied Polymer Science*, *24*, 1073.

Sarkar, N., & Walker, L. C. (1995). Hydration–dehydration properties of methylcellulose and hydroxypropyl methyl cellulose. *Carbohydrate Polymers*, *27*, 177.

Wang, G., Lindwell, K., & Olofsson, G. (1997). On the thermal gelling of ethyl(hydroxy ethyl) cellulose and sodium dodecyl sulphate, phase behavior and temperature scanning calorimetric response. *Macromolecules*, *30*, 105.