Hydrophobic hydration of hydroxyalkyl cellulose

Shinobu Koda*, Takeo Hori and Hiroyasu Nomura
Department of Chemical Engineering, School of Engineering, Nagoya University, Chikusa-ku, Nagoya 464-01, Japan

(Received 24 July 1991; revised 1 September 1991; accepted 20 September 1991)

Measurements of sound velocity and solution density of hydroxyalkyl cellulose have been carried out at temperatures of 15, 25 and 35°C. The partial molar volume and partial molar adiabatic compressibility of hydroxyalkyl cellulose have been evaluated from these data as a function of molar substitution. The partial molar volume of hydroxyethyl and hydroxypropyl cellulose increased with the molar substitution, but they were independent of temperature. The partial molar adiabatic compressibility of hydroxyalkyl celluloses depends strongly on the structure of the substituted group and the molar substitution. The compressibility data indicate that hydroxypropyl cellulose shows a strong hydrophobic character but hydroxyethyl cellulose a weak hydrophilic one.

(Keywords: hydrophobic hydration; hydroxypropyl cellulose; hydroxyethyl cellulose; adiabatic compressibility; sound velocity)

INTRODUCTION

The macroscopic solution properties, such as viscosity, of water-soluble cellulose derivatives depend on the molecular weight, solute concentration and temperature. Thermal gelation also leads to a change of viscosity of the solution, which is interpreted in terms of a change of the local structure of the solute and hydrophobic and hydrophilic solute–solvent interactions. The structure of the substituted group and the degree of substitution are the most important factors to determine the solubility and the hydration nature of the cellulose derivatives. In previous papers[1,2], the hydration behaviour of carboxymethyl and methyl cellulose was investigated by measurement of the partial molar volume and partial molar compressibility. Additivity of the partial molar volume of the substituted groups held for both cellulose derivatives. The amounts of hydration of carboxymethyl cellulose increased with the degree of substitution of the hydrophilic $-CH_2COONa$ group, but that of methyl cellulose decreased with the hydrophobic $-CH_3$ group. The hydration behaviour of the hydrophilic site in cellulose derivatives is quite different from that of the hydrophobic one.

Hydroxyalkyl cellulose has a hydrophobic alkyl group and hydrophilic OH group in a glucose unit. The solubility in water and the solution viscosity of hydroxyalkyl cellulose are different from those of methyl cellulose. The physicochemical properties of the hydroxyalkyl celluloses in aqueous solution can be controlled by changing the ratio of the hydrophobic and hydrophilic groups. It is instructive to investigate the contribution of the hydrophobic and hydrophilic sites to the hydration nature of hydroxyalkyl cellulose derivatives. The purpose of this work is to investigate the hydration nature of hydroxyethyl and hydroxypropyl celluloses by measurement of the partial molar volume and partial molar adiabatic compressibility. A discussion on the hydrophobic hydration of these compounds on the basis of the obtained data will be carried out in comparison with the results of methyl cellulose reported previously.

EXPERIMENTAL

Samples

Hydroxyethyl cellulose (HEC), hydroxyethylmethyl cellulose (HEMC), hydroxypropyl cellulose (HPC) and hydroxypropylmethyl cellulose (HPMC) with different degrees of substitution were supplied from Shin-Etsu Chemical Co. Ltd. Hereafter, the molar substitution of hydroxyalkyl group and the degree of substitution of methoxy group are abbreviated as *MS* and *DS*, respectively. The *MS* values of the hydroxyalkyl celluloses used here are summarized in *Table 1*. All samples were prepared in the following way. HEC, HEMC and HPMC were precipitated from their aqueous solution into acetone and HPC from hot water. The samples were dialysed against pure water for a week and finally they were freeze-dried around room temperature.

Measurements

The sound velocity was measured with the differential sound velocimeter that we used previously[3,4]. The accuracy in sound velocity was within 1.0 cm s^{-1}. A detailed description of the sound velocity apparatus is given elsewhere.

The solution density was measured by a DMA-02C digitial precision densitometer (Anton Paar Co.). Measurements were carried out at temperatures of 15, 25 and 35°C with precision of ±0.01°C.

---

*To whom correspondence should be addressed

0032-3861/92/153234-05

Table 1 Molar substitution (*MS*) and degree of substitution (*DS*)

Code	*DS*	*MS*
HEC-1		1.87
HEC-2		2.48
HEC-3		3.06
HPC-1		2.65
HPC-2		2.75
HPC-3		3.12
HEMC-1	1.41	0.18
HEMC-2	1.49	0.32
HPMC-1	1.42	0.17
HPMC-2	1.45	0.34
HPMC-3	1.28	0.78

The adiabatic compressibility of the solution, β_s (bar^{-1}), is obtainable from the following Laplace equation:

$$\beta_s = 100/V^2d \qquad (1)$$

where d (g cm^{-3}) and V (m s^{-1}) are the density and sound velocity of the solution, respectively.

The apparent molar volume, ϕ_v, and apparent molar adiabatic compressibility, $\phi_{\kappa s}$, of solute component in solution were calculated by the following conventional equations:

$$\phi_v = 1000(d_0 - d)/md_0d + M/d \qquad (2)$$

and

$$\phi_{\kappa s} = 1000(\beta_s - \beta_{s0})/md_0 + \beta\phi_v \qquad (3)$$

where m is the molality and M is the molar mass of the repeat unit. The subscript 0 refers to the solvent. The molar mass of the repeat unit for cellulose derivatives is given by:

$$M = 161.1 + DS \times 14.0 + MS_E \times 44.1 + MS_P \times 94.1 \qquad (4)$$

where MS_E and MS_P are the molar substitution of hydroxyethyl and hydroxypropyl groups, respectively.

RESULTS

Typical examples of the concentration dependence of the apparent molar volume and adiabatic compressibility are shown in *Figures 1* and *2*, respectively. The apparent molar quantities are nearly independent of the solute concentration. The partial molar quantities at infinite dilution, $\bar{\phi}_v$ and $\bar{\phi}_{\kappa s}$, are estimated by extrapolation of ϕ_v and $\phi_{\kappa s}$ to $m = 0$. The values of $\bar{\phi}_v$ and $\bar{\phi}_{\kappa s}$ thus obtained are summarized in *Tables 2* and *3*.

The partial molar volumes of all samples are independent of temperatures investigated here. This tendency was also observed for carboxymethyl cellulose (CMC)[1] and methyl cellulose (MC)[2]. In *Figure 3* are shown the partial molar volumes of hydroxyalkyl celluloses as a function of *MS* at 25°C, together with the result for MC, which is plotted against *DS*. The $\bar{\phi}_v$ for all samples increases linearly with *MS* or *DS*. The partial molar volume of the derivatives obtained by extrapolating ϕ_v to $MS = 0$ corresponds to that of the hypothetical cellulose unit dissolved in water (93.1 cm^3 mol^{-1}), which has been estimated previously. The $\bar{\phi}_v$ obtained by extrapolating the content of the hydroxyalkyl group in HEMC and HPMC to zero is consistent with that of MC if the methoxy contents in HEMC and HPMC are the same as that in MC. The $\bar{\phi}_v$ per substituted group estimated from the slope in *Figure 3* for HEC and HPC are 37.5 and 58.5 cm^3 mol^{-1}, respectively. If the partial molar volume of a methoxy group is assumed to be unchanged by introduction of a hydroxyalkyl group, the $\bar{\phi}_v$ of hydroxyethyl and hydroxypropyl groups obtained from the slope for HEMC and HPMC in *Figure 3* are 20.0 and 44.0 cm^3 mol^{-1}, respectively.

Figure 4 shows the temperature dependence of the partial molar adiabatic compressibilities of HEC and HPC in aqueous solution. For comparison, the values of $\bar{\phi}_{\kappa s}$ of MC, which have been previously reported, are also shown in *Figure 4*. The value of $\bar{\phi}_{\kappa s}$ increases with

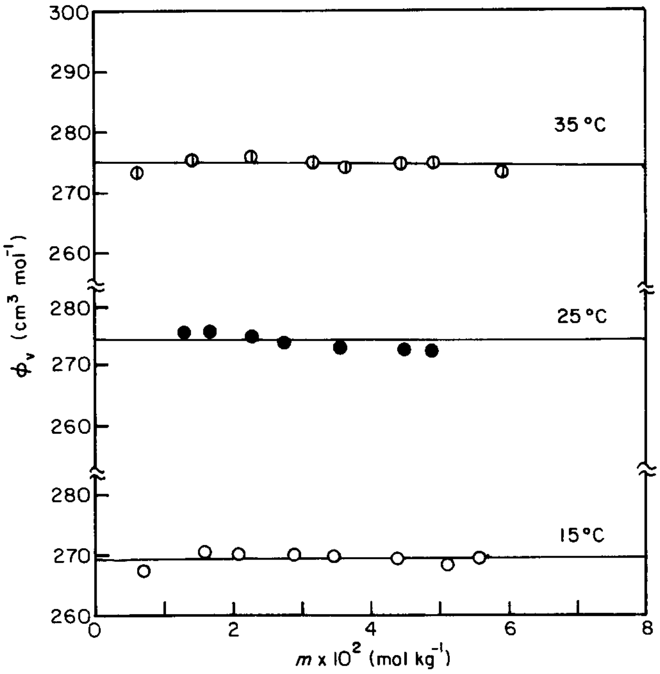

Figure 1 Plots of apparent molar volume *versus* concentration for HPC with *MS* = 3.12 at 15, 25 and 35°C

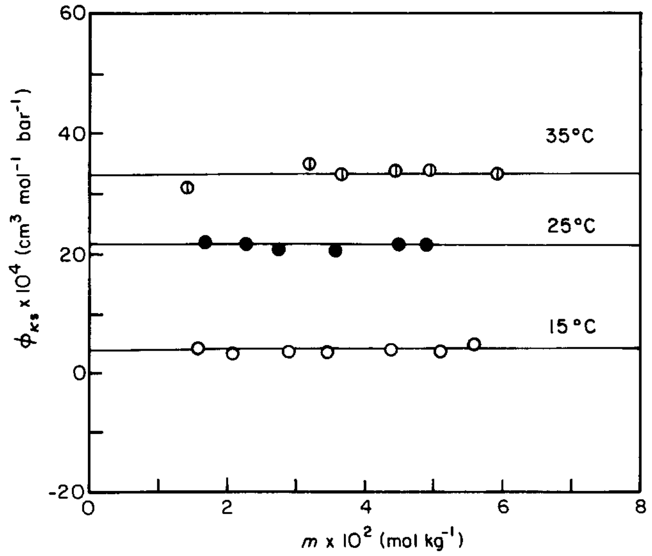

Figure 2 Plots of apparent molar adiabatic compressibility *versus* concentration for HPC with *MS* = 3.12 at 15, 25 and 35°C

Table 2 Partial molar volume of HEC, HPC, HEMC and HPMC ($cm^3 mol^{-1}$) at 15, 25 and 35°C

Code	15°C	25°C	35°C
HEC-1	164.7	165.5	164.0
HEC-2	190.0	188.3	188.5
HEC-3	208.9	207.3	207.4
HPC-1	238.8	243.0	243.3
HPC-2	247.6	249.1	251.2
HPC-3	269.3	273.3	273.9
HEMC-1	132.5	132.8	132.9
HEMC-2	134.8	133.3	136.3
HPMC-1	132.5	133.2	132.4
HPMC-2	144.8	145.2	145.2
HPMC-3	162.3	163.2	164.2

Table 3 Partial molar adiabatic compressibility of HEC, HPC, HEMC and HPMC (10^{-4} $cm^3 mol^{-1} bar^{-1}$) at 15, 25 and 35°C

Code	15°C	25°C	35°C
HEC-1	−11.3	−1.9	−1.3
HEC-2	−11.0	−2.7	3.5
HEC-3	−12.0	−3.3	6.2
HPC-1	−4.2	7.9	16.1
HPC-2	−3.6	9.7	24.8
HPC-3	3.3	21.8	33.3
HEMC-1	−6.5	−1.9	4.7
HEMC-2	−8.4	−4.7	2.2
HPMC-1	−9.2	−1.9	1.6
HPMC-2	−6.5	0.52	6.8
HPMC-3	−9.4	0.71	7.2

MS and temperature. The value of $\bar{\phi}_{KS}$ of HPC shows the strongest temperature dependence among the hydroxyalkyl celluloses investigated here.

The temperature dependences of $\bar{\phi}_{KS}$ of HEMC and HPMC are shown in *Figure 5*. The $\bar{\phi}_{KS}$ of MC with the corresponding degree of substitution ($DS = 1.4$–1.5) is also shown in *Figure 5*. The introduction of a small number of hydroxypropyl groups into MC ($DS = 1.4$) has almost no effect on the $\bar{\phi}_{KS}$ of MC, but the introduction of hydroxyethyl groups into MC leads to a slight decrease of $\bar{\phi}_{KS}$.

Figure 6 shows the effect of the substituted group on the $\bar{\phi}_{KS}$ at 25°C. The $\bar{\phi}_{KS}$ depends on the structure of the substitution groups. The $\bar{\phi}_{KS}$ of HEC decreases slightly with the molar substitution but the $\bar{\phi}_{KS}$ of HPC increases abruptly with the molar substitution, especially above $MS = 2.5$. The partial introduction of hydroxyethyl groups into MC results in the decrease of the $\bar{\phi}_{KS}$ but the $\bar{\phi}_{KS}$ of HPMC remains unchanged by the introduction of the hydroxypropyl group.

DISCUSSION

In previous papers[1,2], it was found that the partial molar volume of CMC and MC increased linearly with the degree of substitution of $-CH_2COONa$ or $-CH_3$. In the case of HEC and HPC, the same additivity for the partial molar volume of hydroxyalkyl groups is observed. The $\bar{\phi}_v$ of HEMC and HPMC increased linearly with increasing content of hydroxyalkyl group in the repeat unit, but the $\bar{\phi}_v$ per hydroxyalkyl group of HEMC and HPMC is smaller than those obtained from HEC and HPC.

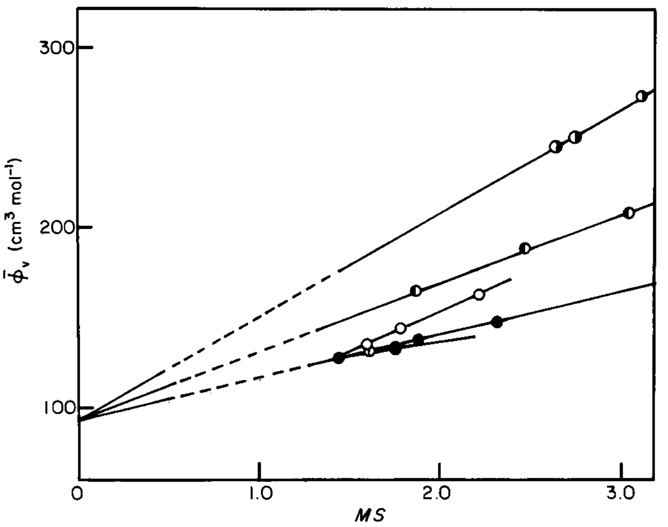

Figure 3 Partial molar volume of hydroxyalkyl cellulose in water at 25°C plotted as a function of *MS*: HEC (◐), HPC (◑), HEMC (⦶), HMPC (○) and MC (●)

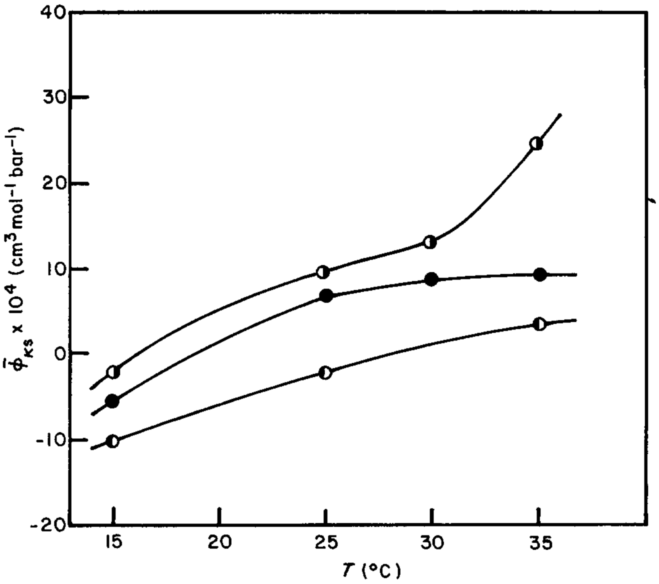

Figure 4 Temperature dependence of partial molar adiabatic compressibility of HEC-2 (◐), HPC-2 (◑) and MC ($DS = 1.89$, ●) samples

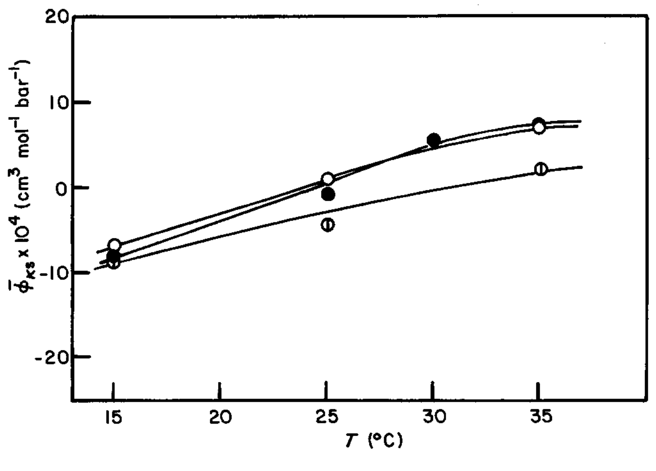

Figure 5 Temperature dependence of partial molar adiabatic compressibility of HEMC-2 (⦶), HPMC-2 (○) and MC ($DS = 1.49$, ●) samples

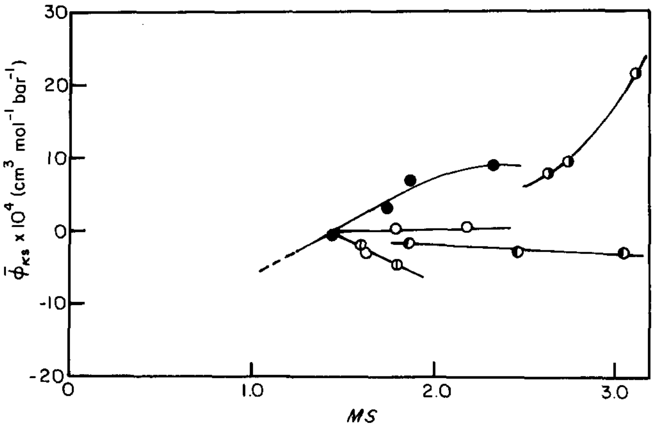

Figure 6 Partial molar adiabatic compressibility of HEC (◐), HPC (◑), HEMC (⦶), HPMC (○) and MC (●) in water at 25°C plotted as a function of *MS*

The additivity of the partial molar volume of the functional group has been discussed by many workers. The partial molar volume of a non-ionic polymer in solution can be estimated from the group contribution to the partial molar volume[5–8]. Zana gives the partial molar volumes of $-CH_3$ (26.7 cm^3 mol^{-1}), $-CH_2-$ (16.0 cm^3 mol^{-1}), $-CH=$ (5.3 cm^3 mol^{-1}), $-O-$ (4.1 cm^3 mol^{-1}) and so on for a non-ionic polymer in aqueous solution. HEC is a polymer obtained by substituting the $-H$ in the $-OH$ group of cellulose by the $-C_2H_4OH$ group[6]. The increase of the partial molar volume of HEC with *MS* is ascribed to that of the $-C_2H_4O-$ group. The partial molar volume calculated from the group contribution reported by Zana[6], $\bar{\phi}_{\rm v}$(calc), is 36.1 cm^3 mol^{-1} for the $-C_2H_4O-$ group. The $\bar{\phi}_{\rm v}$(calc) of the $-C_2H_4O-$ group is in good agreement with the $\bar{\phi}_{\rm v}$(expt) estimated from HEC. The partial molar volume calculated from the group contribution is 52.1 cm^3 mol^{-1} for the $-C_3H_6O-$ group, which is smaller than the $\bar{\phi}_{\rm v}$(expt) of the $-C_3H_6O-$ group. In the calculation of $\bar{\phi}_{\rm v}$(calc), 5.3 cm^3 mol^{-1} is used as the value of $\bar{\phi}_{\rm v}$ of the $-CH$ group. French and Criss have reported 8.8 cm^3 mol^{-1} as the $\bar{\phi}_{\rm v}$ of the $-CH$ group for propylene carbonate in water[7], and Jolicoeur and Lacroix have reported 12.0 cm^3 mol^{-1} as the $\bar{\phi}_{\rm v}$ of the $-CH$ group for alcohol in water[5]. If one uses 8.8 or 12.0 cm^3 mol^{-1} as the $\bar{\phi}_{\rm v}$ of the $-CH$ group, the $\bar{\phi}_{\rm v}$ of the $-C_3H_6O-$ group is evaluated as 55.6 or 58.8 cm^3 mol^{-1}. The $\bar{\phi}_{\rm v}$(expt) estimated from *Figure 3* lies within the calculated values. As the additivity of the group contributions holds well for MC, CMC and HEC, it is reasonable that the same thing is true for HPC. The values of $\bar{\phi}_{\rm v}$ of the $-CH$ group in $-C_2H_4O-$ and $-C_3H_6O-$ groups may be in the range from 8 to 12 cm^3 mol^{-1}.

The values of $\bar{\phi}_{\rm v}$ of the $-C_2H_4O-$ and $-C_3H_6O-$ groups estimated from HEMC and HPMC data are decreased by 17.5 and 13.5 cm^3 mol^{-1}, respectively, compared with the results of HEC and HPC. The decrease of $\bar{\phi}_{\rm v}$ of $-C_2H_4O-$ and $-C_3H_6O-$ groups for HEMC and HPMC means that there is an interaction between the methoxy and hydroxyalkyl groups. The $-CH_3$ group in the methoxy group is influenced by the adjacent $-OH$ group in the hydroxyalkyl group. Consequently, the environments around the $-CH_3$ and $-OH$ groups are perturbed by one another. A weak interaction between $-CH_3$ groups in methoxy group and hydroxypropyl group may exist since the decrement of the $\bar{\phi}_{\rm v}$ of the $-C_3H_6O-$ group in HPMC is different from that of the $-C_2H_4O-$ group in HEMC.

The $\bar{\phi}_{\kappa s}$ of solute in aqueous solutions is ascribed to the partial molar adiabatic compressibility of solute itself and the solute–solvent interaction, that is hydration. The $\bar{\phi}_{\kappa s}$ of the solute itself, that is the $\bar{\phi}_{\kappa s}$ of the dehydrated state, can be obtained by substituting water molecules by ethanol (the alcohol precipitation method)[9]. However, it is difficult to obtain the $\bar{\phi}_{\kappa s}$ related to the dehydrated state of hydroxyalkyl celluloses, since the cellulose derivatives are highly soluble in alcohol.

Similar to the investigation of the partial molar volume, the group contributions of $\bar{\phi}_{\kappa s}$ and their temperature dependence have been discussed[10–16]. Harada *et al.* have studied the partial molar adiabatic compressibility of alkoxyethanols in aqueous solutions. They indicated that the $\bar{\phi}_{\kappa s}$ of $-CH_2-$ and $-CH_3$ in aqueous solution is negative at low temperatures and increases with temperature. As is shown in *Figure 4*, the $\bar{\phi}_{\kappa s}$ of HPC shows a more marked temperature dependence above ca. 30°C. The $\bar{\phi}_{\kappa s}$ of HEC with the higher *MS* increases slightly with temperature. The magnitude of the $\bar{\phi}_{\kappa s}$ of the substituted groups in cellulose derivatives is in the order $-C_3H_6OH > -CH_3 > -C_2H_4OH$ at 35°C. The $\bar{\phi}_{\kappa s}$ of $-CH_2$ and $-CH_3$ are reported as -1.3×10^{-4} and 1.8×10^{-4} cm^3 mol^{-1} bar^{-1} at 25°C and 2.1×10^{-4} and 8.2×10^{-4} cm^3 mol^{-1} bar^{-1} at 45°C, respectively. The highest value of $\bar{\phi}_{\kappa s}$ of HPC at 35°C is due to the increase of $\bar{\phi}_{\kappa s}$ of the hydrophobic $-CH_3$ group. In the case of HEC without the $-CH_3$ group, only the $-CH_2-$ group contributes to the $\bar{\phi}_{\kappa s}$ and, consequently, a weak temperature dependence is observed. As pointed out previously[2], the $\bar{\phi}_{\kappa s}$ of MC is almost independent of temperature above ca. 25°C, since MC is dehydrated with increasing temperature.

Hydroxyalkyl cellulose has three OH groups in a cellulose unit even if an OH group is substituted by a hydroxyalkyl group. However, the OH group in MC is decreased with increase of the methoxy content. Therefore, the variation of $\bar{\phi}_{\kappa s}$ of HEC and HPC against *MS* is caused by the increase of the $-C_2H_4O-$ and $-C_3H_6O-$ groups, respectively. As is shown in *Figure 6*, the $-C_2H_4O-$ group has a negative effect on $\bar{\phi}_{\kappa s}$ but the $-C_3H_6O-$ has a positive one. The introduction of a $-C_2H_4O-$ group into the cellulose unit enhances the hydration. In the case of HEC, the hydrophilic nature of the OH group is superior to the hydrophobic one of the $-C_2H_4-$ group. On the other hand, HPC shows strong hydrophobicity, which is superior to the hydrophilic nature of the OH group.

The introduction of a small amount of $-C_3H_6O-$ groups into MC does not affect the hydration behaviour of MC, as shown in *Figure 5*. In other words, the hydration behaviour is intrinisically unchanged by the introduction of hydroxypropyl groups. Nakamura *et al.* have studied the temperature dependence of the viscosity of 2% aqueous solutions of HPC, HPMC and MC[17]. The introduction of a small amount of hydroxypropyl groups into MC results in a slight decrease of the viscosity of its solution, but the temperature dependence of viscosity of HPMC solution is similar to that of MC, that is, the viscosities of MC and HPMC solutions decrease linearly with temperature up to ca. 60°C. Below that temperature, the partial molar volume and the viscosity of solution of MC is not so affected by the inroduction of a $-C_3H_6O-$ group. Above ca. 60°C the viscosity of MC solution increases abruptly with increasing temperature but that of HPMC solution still decreases sharply and above ca. 75°C increases[17]. The dehydration of MC and HPMC in aqueous solution is prompt with increasing temperature. Therefore, the interaction between the hydrophobic groups in the dehydrated state dominates the temperature dependence of viscosity of solutions.

The $\bar{\Phi}_{KS}$ of HEMC decrease by introduction of the $-C_2H_4O-$ group into MC, as shown in *Figure 5*. The decrease of $\bar{\Phi}_{KS}$ is ascribed to the increase of the hydrophilic hydration of HEMC, since the hydroxyethyl group shows slightly hydrophilic hydration, as observed for HEC.

ACKNOWLEDGEMENTS

The authors wish to thank Shin-Etsu Chem. Ind. for supplying the methyl cellulose samples. This work was supported in part by a Grant-in-Aid for Scientific Research on Priority Area (No. 03231102) from the Ministry of Education, Science and Culture, Japan.

REFERENCES

1 Koda, S., Hasegawa, S., Mikuriya, M., Kawaizumi, F. and Nomura, H. *Polymer* 1988, **29**, 2188

2 Koda, S., Hori, T., Kawaizumi, F. and Nomura, H. *Polymer* 1991, **32**, 2806

3 Nomura, H., Koda, S., Matsumoto, K. and Miyahara, Y. in 'Ions and Molecules in Solutions' (Eds H. Ohtaki and R. Tamamushi), Elsevier, Amsterdam, 1982, p. 151

4 Kawaizumi, F., Matsumoto, K. and Nomura, H. *J. Phys. Chem.* 1983, **87**, 3161

5 Jolicoeur, C. and Lacroix, G. *Can. J. Chem.* 1976, **54**, 624

6 Zana, R. *J. Polym. Sci., Polym. Phys. Edn.* 1980, **18**, 121

7 French, R. N. and Criss, C. M. *J. Solution Chem.* 1981, **10**, 713

8 Mishra, A. K. and Ahluwalia, J. C. *J. Phys. Chem.* 1984, **88**, 86

9 Miyahara, H. and Shiio, H. *Nippon Kagaku Zasshi* 1951, **72**, 876

10 Nakajima, T., Komatsu, T. and Nakagawa, T. *Bull. Chem. Soc. Jpn* 1975, **48**, 783

11 Harada, S., Nakajima, T., Komatsu, T. and Nakagawa, T. *J. Solution Chem.* 1978, **7**, 463

12 Hoiland, H. and Vikingstud, E. *Acta Chem. Scand.* (*A*) 1976, **30**, 182

13 Hoiland, H. *J. Solution Chem.* 1980, **9**, 857

14 Cabani, S., Conti, G. and Mattroli, E. *J. Solution Chem.* 1979, **8**, 11

15 Juszkiewicz, A. and Antosiewicz, J. *Z. Phys. Chem.* 1986, **148**, 185

16 Iqbal, M. and Verral, R. E. *J. Phys. Chem.* 1987, **91**, 967

17 Nakura, S., Nakamura, S. and Onda, Y. *Koubunshi Ronbunshu* 1981, **38**, 133