Hydration of methyl cellulose

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Measurements of the sound velocity in and density of solutions of methyl cellulose have been carried out at various temperatures (15, 25, 30 and 35°C). The partial molar volume and partial molar adiabatic compressibility of methyl cellulose have been evaluated from these data as a function of degree of substitution, i.e. the average number of $-OCH_3$ groups in a glucose unit. The partial molar volume of methyl cellulose increased with the degree of substitution but it was independent of temperature. The amount of hydration of methyl cellulose was calculated after evaluating the compressibility of the dehydrated methyl cellulose, which was estimated from the temperature dependence of the partial molar adiabatic compressibility. The hydration number of methyl cellulose decreased with the degree of substitution.

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

INTRODUCTION

Water-soluble cellulose derivatives, which are obtained by introducing hydrophobic or hydrophilic substituents into cellulose molecules, are widely used in various industrial areas. Their solubility in water is an important factor that dominates the physicochemical properties of their solutions and, therefore, the extent of practical utility of cellulose derivatives. The dissolution of solute in water is obviously intimately related to the hydration of the solute molecules. The solubility of cellulose derivatives varies with the kind of substituents, the degree of substitution and, more strictly speaking, with the distribution of the substituents in the backbone chain of the cellulose molecules. The basic constituent unit of cellulose is glucopyranose, which shows both hydrophilic and hydrophobic interactions, respectively due to –OH groups and –CH and $-CH_2$ groups. The introduction of substituents such as $-OCH_3$, $-OC_2H_5$, $-OCH_2COONa$ and $-OSO_3Na$ enhances the hydrophobic or hydrophilic properties of cellulose. It has been demonstrated by a number of experimental studies that, even for the most simple case of glucose, hydration consists of hydrophilic and hydrophobic hydrations. The hydration behaviour of glucose and glucose derivatives has been reviewed elsewhere[1–3].

Quite a number of papers have been published on the hydration of carbohydrates. However, most of them are concerned with the results of partial molar volumes[4–7]. In addition, papers on the hydration of cellulose derivatives are very rare[8]. In our previous paper[9], the hydration of carboxymethyl cellulose (CMC) and carboxymethyl dextran (CMD) was investigated from the point of view of adiabatic compressibility of the solution. The adiabatic compressibility is obtainable from measurements of the sound velocity in and density of the medium for sound propagation. Using the compressibility data obtained, we calculated the amounts of hydration of CMC and CMD as a function of degree of substitution[9]. Our previous work has shown that the hydration of CMC and CMD consists of two parts: one is hydration inherent to cellulose and dextran structure, and the other is due to the hydrophilic character of the substituting radical $-CH_2COONa$. Hydrated water molecules of the latter are numerically the same for CMC and CMD.

Methyl cellulose (MC) is one of the most familiar cellulose derivatives. It dissolves easily in water at low temperatures, showing that the hydration of MC is strongly hydrophobic in nature. The purpose of this work is to evaluate the hydration number of MC as a function of degree of substitution, i.e. the number of $-OCH_3$ groups in a cellulose unit. Among the various methods available to evaluate the amount of hydration, we adopted the compressibility method, which has been widely applied to determine the hydration number of both electrolytes and non-electrolytes. The hydrophobic hydration of MC will be discussed through comparison with the hydrophilic hydration of CMC and CMD mentioned previously[9].

EXPERIMENTAL

Samples

Methyl celluloses with different degrees of substitution were supplied by Shin-Etsu Chemical Co. Ltd. The degrees of substitution of the four samples used determined by the Zeisel method are 1.45, 1.76, 1.89 and 2.34. MCs were purified by precipitation from their hot aqueous solution, since MC becomes more insoluble with increasing temperature. All 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 same

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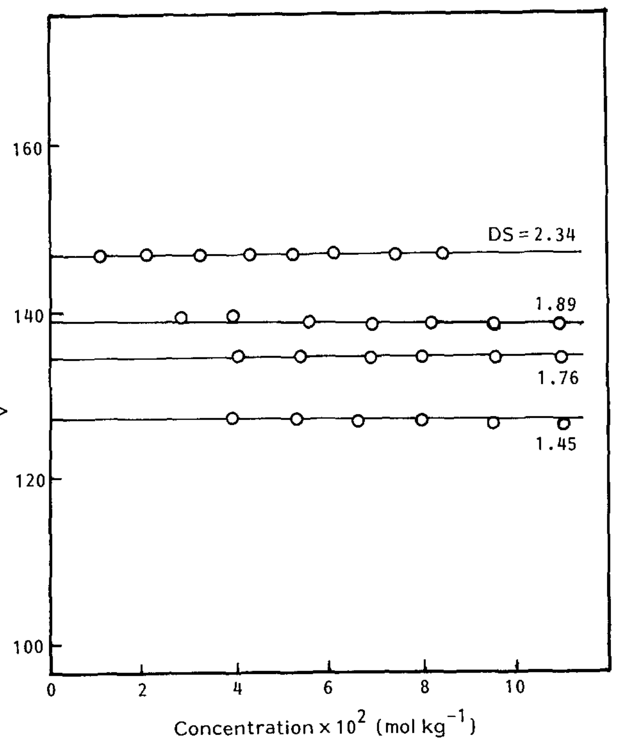

Figure 1 Plots of apparent molar volume *versus* concentration for MC with different degrees of substitution dissolved in water at 25°C

differential sound velocimeter that we used previously[9]. The accuracy of sound velocity was within 1.0 cm s^{-1}. A detailed description of the sound velocity apparatus is given elsewhere[10,11].

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

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

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

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

Treatment of data

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

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

and

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

where in both equations m is the molality and M the molar mass of the repeat unit. The subscript 0 refers to the solvent.

Similarly as in our previous work[9], we used the following relation to determine the hydration number of a solute in solution:

$$n_h = \frac{\bar{\phi}_{\kappa s}(h) - \bar{\phi}_{\kappa s}(d)}{\bar{\phi}_{vw}(\beta_h - \beta_w)} \qquad (4)$$

where $\bar{\phi}_{\kappa s}(h)$ is the partial molar adiabatic compressibility of a hydrated solute, $\bar{\phi}_{\kappa s}(d)$ that of a dehydrated solute, β_w the adiabatic compressibility of water, β_h the adiabatic compressibility of the hydrated water and $\bar{\phi}_{vw}$ the partial molar volume of water.

RESULTS

Figures 1 and *2* show respectively the concentration dependence of the apparent molar volume and apparent molar adiabatic compressibility of the MC samples with different degrees of substitution (hereafter abbreviated as *DS*) at 25°C. Both apparent molar quantities are almost independent of concentration for all the samples investigated. 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 $m = 0$. In *Figures 1* and *2*, the extrapolation can be done very easily. The values of $\bar{\phi}_v$ and $\bar{\phi}_{\kappa s}$ thus obtained are summarized in *Tables 1* and *2*, together with the experimental results obtained at 15, 30 and 35°C.

In *Figure 3* are shown the partial molar volumes of methyl cellulose as a function of *DS*. The $\bar{\phi}_v$ value increases linearly with *DS* but it is independent of temperature within experimental errors. This tempera-

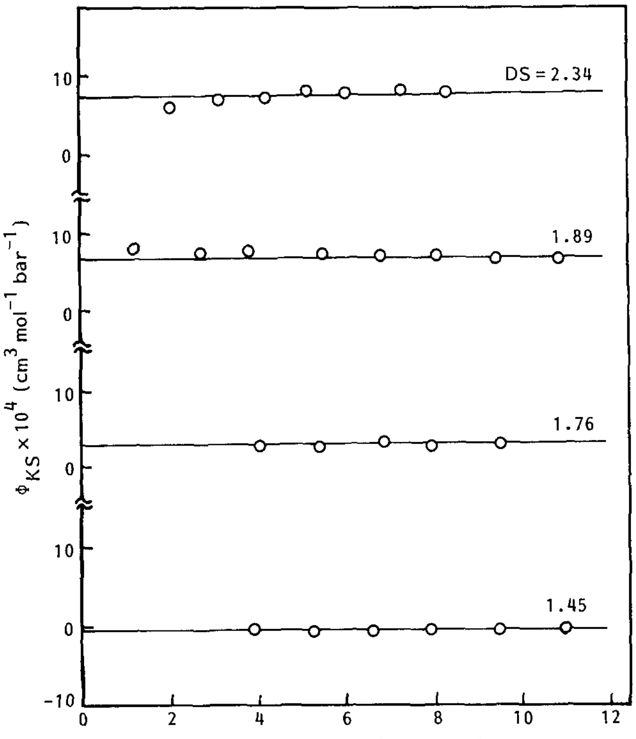

Figure 2 Plots of apparent molar adiabatic compressibility *versus* concentration for MC with different degrees of substitution in water at 25°C

Table 1 Partial molar volume (cm^3 mol^{-1}) of MC at various temperatures

T	Degree of substitution			
(°C)	1.45	1.76	1.89	2.34
15	129.0	133.0	135.8	146.0
25	128.2	134.5	138.6	147.3
30	127.6	133.6	136.5	–
35	129.1	134.1	136.3	–

Table 2 Partial molar adiabatic compressibility (10^{-4} cm^3 mol^{-1} bar^{-1}) of MC at various temperatures

T (°C)	Degree of substitution 1.45	1.76	1.89	2.34
15	−7.70	−4.55	−4.40	−1.82
25	−0.63	3.15	6.95	7.74
30	5.83	7.00	8.67	–
35	7.34	8.48	8.80	–

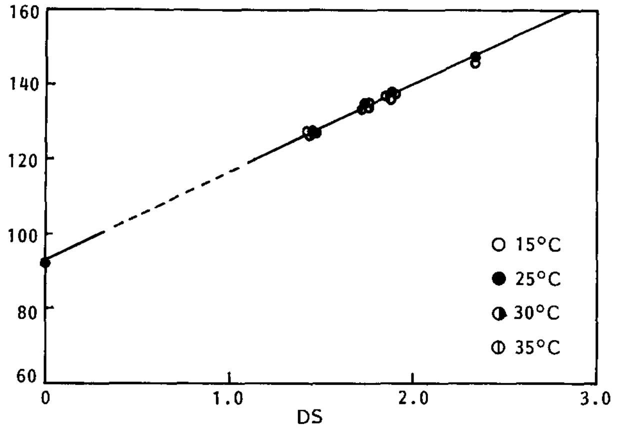

Figure 3 Partial molar volume of MC in water at 15, 25, 30 and 35°C plotted as a function of *DS*

ture-independent behaviour will be discussed below. The *DS* dependence of $\bar{\phi}_v$ is expressed as:

$$\bar{\phi}_v = 93.1 + 23.5DS \qquad (5)$$

The partial molar volume of MC at $DS = 0$ gives the partial molar volume of the hypothetical cellulose unit dissolved in water. The value of the partial molar volume of the cellulose unit obtained here (93.1 cm^3 mol^{-1}) is in good agreement with the one (92.4 cm^3 mol^{-1}) obtained previously[9] from the result of *DS* dependence of carboxymethyl cellulose.

Figure 4 shows the partial molar adiabatic compressibilities of MC in aqueous solution as a function of *DS*. The value of $\bar{\phi}_{KS}$ increases with *DS* and temperature. As the temperature increases, the increment of $\bar{\phi}_{KS}$ becomes smaller, and above 30°C, the value of $\bar{\phi}_{KS}$ progressively approaches a constant value, irrespective of *DS*. At 35°C, $\bar{\phi}_{KS}$ is effectively independent of *DS*.

DISCUSSION

The partial molar volume of MC increases linearly with the degree of substitution, as shown in *Figure 3*. This result indicates the additivity of the partial molar volume of MC with respect to *DS*. The partial molar volumes of glucose and α-methylglucose are 111.7[6] and 133.2[4] cm^3 mol^{-1}, respectively. Therefore, the difference between these two values, 21.5 cm^3 mol^{-1}, corresponds to the increment of the partial molar volume due to the substitution of an –OH group in a glucose unit by an –OCH$_3$ group. The increment of the partial molar volume estimated from the slope in *Figure 3* is 23.5 cm^3 mol^{-1}. The good agreement for the increment of $\bar{\phi}_v$ indicates that the contribution of the –OCH$_3$ group to the partial molar volume of MC is the same for the case of mono-substituted glucose. Zana[12,13] reported the values of group contributions to the partial molar volume of non-ionic polymers in water. According to his result, the increment of partial molar volume associated with the substitution of –OH by –OCH$_3$ amounts to 18.8 cm^3 mol^{-1}. Harada *et al.*[14] have shown that the partial molar volumes of the hydrophobic groups in a series of ethyleneglycol derivatives are affected by the location of the –OH group. In a molecule of methyl cellulose, the –OH group is in the vicinity of the –CH– group and these two groups affect each other. This is sufficient for interpreting that the value obtained for the cellulose derivative is slightly larger than that based on the values listed by Zana[13].

As is seen in *Figure 3*, the partial molar volumes of MC are independent of the temperature ranges investigated here. The temperature derivative of the partial molar volume at constant pressure is the partial molar expansibility, which, for example, for a typical non-electrolyte solute, urea, in water at 27.5°C ($\bar{\phi}_v = 44.385$ cm^3 mol^{-1}), is reported[15] as 0.0645 cm^3 mol^{-1} K^{-1}. It seems appropriate to consider that the partial molar volume of non-electrolyte consists of the following three parts: contribution from the intrinsic volume of solute, effect of hydrophilic hydration and that of hydrophobic hydration. Therefore, the partial molar expansibility also consists of the same three parts. However, in taking account of the smallness of the partial molar expansibility in general and the temperature ranges concerned in this work, what is certain for the temperature variation of the partial molar volumes given in *Table 1* is that the observed values are of the correct order of magnitude. More precise determination of $\bar{\phi}_v$ in more extended temperature ranges would be needed for a detailed discussion or estimation of hydrophilic hydration and hydrophobic hydration as a function of the $\bar{\phi}_v$ values.

The partial molar adiabatic compressibility of MC varies not only with *DS* but also with temperature. In our previous paper[9], we applied the alcohol precipitation method[16–18] in order to estimate the $\bar{\phi}_{KS}$ of dehydrated CMC. This method is based on the assumption that the decrease of solubility of saccharides in water on addition of ethanol to aqueous saccharide solutions results from the dehydration of saccharides, and the precipitation point indicates the appearance of completely dehydrated saccharide molecules in water. However, in the case of

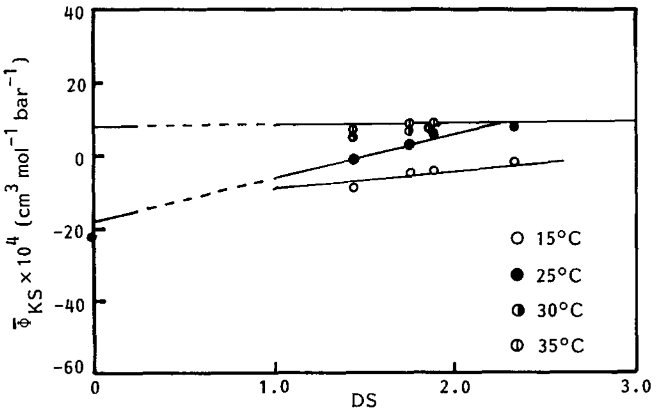

Figure 4 Partial molar adiabatic compressibility of MC in water at 15, 25, 30 and 35°C plotted as a function of *DS*

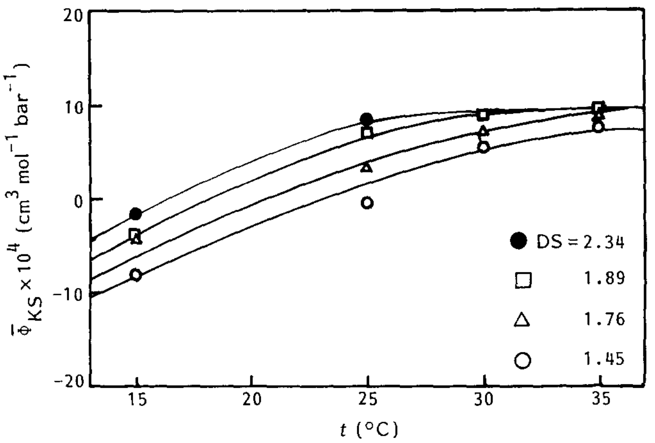

Figure 5 Variation of partial molar adiabatic compressibility of various MC samples with temperature

MC, the alcohol precipitation method is inapplicable on account of the high solubility of MC in alcohols. The MC becomes sparingly soluble with increasing temperature and it is precipitated above ~40°C. We have paid attention to this fact. *Figure 5* shows the temperature dependence of $\bar{\phi}_{KS}$ of MC. With a rise in temperature, the $\bar{\phi}_{KS}$ value increases from negative to positive, and it gradually approaches a constant value, which is taken to be the $\bar{\phi}_{KS}$ of the dehydrated MC molecule, or $\bar{\phi}_{KS}(\mathrm{d})$ of equation (4). The shapes shown in *Figure 5* are quite similar to those observed for the $\bar{\phi}_{KS}$ of dextran plotted against the ethanol contents in the solvent system[19]. In other words, the alcohol precipitation method and the temperature-rise precipitation method are complementary. The averaged $\bar{\phi}_{KS}$ value for the dehydrated MC, 10×10^{-4} cm^3 mol^{-1} bar^{-1}, is slightly larger than that (5.1×10^{-4} cm^3 mol^{-1} bar^{-1}) estimated for dextran by the alcohol precipitation method[19]. However, the fact that the two independent methods lead to roughly the same result indicates the validity of the two methods for the estimation of the compressibility of the dehydrated solute in solution. This in turn proves the usefulness of equation (4), which is based on our simple hydration model re-examined recently[20].

Figure 6 shows the amount of hydration of MC as a function of *DS* calculated using equation (4). In the calculation, the value of β_h was assumed to be that of ice, i.e. 11.1×10^{-6} bar^{-1}, similarly as in our previous work[9]. One may consider that water molecules in the state of hydrophobic hydration are linked together more loosely than for those in the crystallized state, and therefore the compressibility is higher than that of ice. On the other hand, the compressibilities of ordinary organic polymer solids are in the range $(19\text{–}25)\times10^{-6}$ bar^{-1}. If twice the value of the compressibility of ice, 22.2×10^{-6} bar^{-1}, is inserted for β_h in equation (4), then we have amounts of hydration of MC that are one-and-a-half times larger than those plotted in *Figure 6*. But in such a case the extrapolation of n_h to $DS=0$ fails to give the same numerical value derived from the *DS* dependence of CMC, and one is forced to explain the discrepancy of the two extrapolated values, for the state $DS=0$ for CMC means identically the cellulose molecule. Even taking account of the errors due to extrapolation in *Figure 6*, we can say that the compressibility of the layer of hydrophobic hydration does not differ significantly from that of ice.

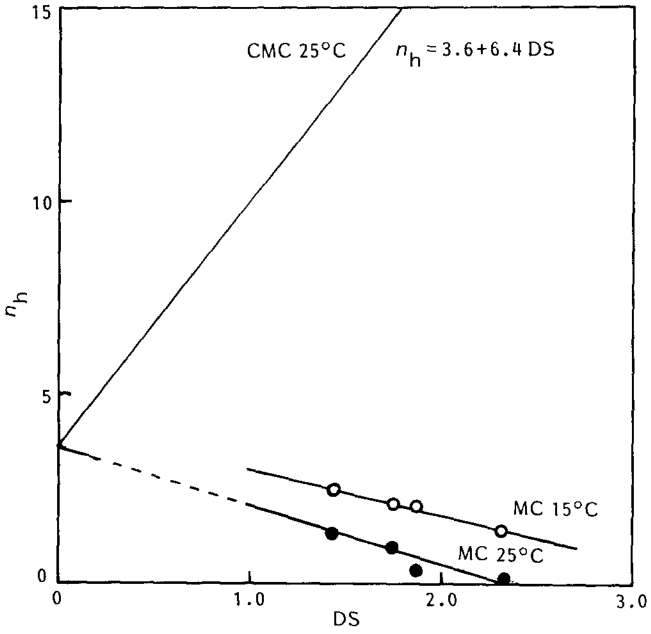

Figure 6 Hydration number (n_h) of MC and CMC as a function of *DS*

The hydration of MC decreases with *DS*, although in our previous work[9] the amounts of hydration increased with *DS* for CMC and CMD (not included in *Figure 5*). The decrease of n_h with *DS* is by no means affected by the values of β_h used in the calculation. The increase of the hydration of CMC and CMD with increasing *DS* value is ascribable to the hydrophilic group $-CH_2COONa$. On the contrary, the decrease of hydration of MC with *DS* is due to the hydrophobic group $-OCH_3$. The hydrophobic group works against the hydration phenomena detectable with the compressibility method. It is also noteworthy that the decrease of hydration on introduction of the hydrophobic group $-OCH_3$ to the cellulose structure is far less in magnitude in comparison with the increase of hydration on introduction of the hydrophilic group $-CH_2COONa$[9].

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