Hydration of carboxymethyl cellulose and carboxymethyl dextran

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(Received 2 May 1988; accepted 17 May 1988)

From the measurements of sound velocity and density of a solution of carboxymethyl cellulose and carboxymethyl dextran, the hydration numbers of these materials were evaluated as a function of the degree of substitution, that is, the average number of $-CH_2COONa$ groups in a glucose unit. The hydration numbers of both carboxymethyl cellulose and carboxymethyl dextran increase with the degree of substitution. The increment of the hydration numbers for both samples is *ca*. 6.6 per degree of substitution and is interpreted in terms of the increase of the hydrophilic $-CH_2COONa$ group in a glucose unit. A slight difference exists between the hydration numbers of carboxymethyl cellulose and carboxymethyl dextran.

(**Keywords: hydration; carboxymethyl cellulose; carboxymethyl dextran; adiabatic compressibility; sound velocity**)

INTRODUCTION

Cellulose, dextran and their derivatives consist of the same glucose unit. Dextran which is composed of α-1,6-linkages is soluble in water but cellulose formed by β-1,4-linkages is practically insoluble. It is considered that the extremely low solubility of cellulose in water is due to the stable crystalline structure formed by the intermolecular hydrogen bond. The β-1,4-linkage constituting the structure of cellulose is in favour of such bond formation. On the other hand, carboxymethyl cellulose (CMC) and methylcellulose are highly soluble in water. The exceptionally high solubility of these cellulose derivatives is ascribed, respectively, to the introduction of the hydrophilic $-CH_2COONa$ group and the hydrophobic methyl group into the molecular structure of cellulose. It is certain that hydration phenomena play important roles in various solution properties of cellulose and dextran derivatives. The hydration behaviour of oligosaccharides, polysaccharides and so on has been well investigated and the results have been summarized in reviews[1-3]. However, little quantitative discussion has been carried out on the hydration behaviour of cellulose and dextran derivatives.

The adiabatic compressibility of the dissolved solutes, which is evaluated from density and sound velocity in solution, is one of the important physical quantities in determining the amount of hydration of the solutes. The hydration number of simple electrolytes in aqueous solution can be estimated, assuming that simple electrolytes are incompressible. However, this assumption does not hold for highly polymerized materials, since the compressibility of dissolved polymers cannot be set equal to zero. In order to obtain the adiabatic compressibility of the non-electrolytic solute itself, Miyahara and Shiio[4,5], and Shiio[6] used the alcohol precipitation method. They assumed that hydrated water molecules around the solute are displaced by alcohol successively and preferentially with increasing alcohol content in the solvent systems, and near the precipitation point the hydration layer around the solute is fully removed. One can then obtain the adiabatic compressibility of the solute itself from the data of adiabatic compressibility in water–alcohol mixtures. This method has been widely applied for estimating the hydration number of polysaccharides[7,8] and proteins[9].

The purpose of this work is to evaluate the hydration number of carboxymethyl cellulose and carboxymethyl dextran as a function of the degree of substitution. The hydration behaviour will be discussed taking into account the data of partial molar volume.

EXPERIMENTAL

Samples. Carboxymethyl celluloses with different degrees of substitution were supplied by Daicel Chem. Ind. The CMC samples were purified several times by precipitation with methanol from aqueous solution of CMC, and the samples were finally freeze-dried at about room temperature. Carboxymethyl dextran (CMD) samples were prepared by etherification of dextran[10,11]. The original dextran sample was purchased from Pharmacia Fine Chemicals ($M_w = 4 \times 10^4$). Samples with differing degrees of substitution were obtained by changing the number of times the above reaction procedure was repeated. The degree of substitution was determined by the titration method.

Measurements. The sound velocity was measured using the differential sound velocimeter based on the sing-around method. The accuracy of the sound velocity measurements was $1.0\,cm\,s^{-1}$. A detailed description of the apparatus has been presented elsewhere[12,13]. The density of the solution was measured by a DMA-02C digital precision densitometer (Anton Paar Co.). All measurements were carried out at 25.00 ± 0.001°C.

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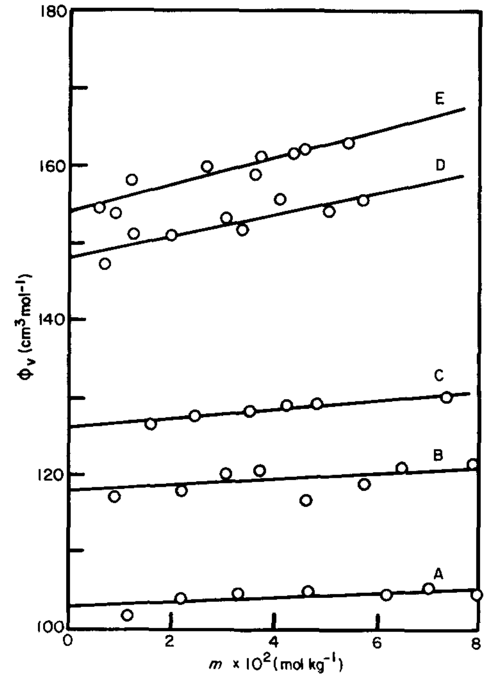

Figure 1 Plots of apparent molar volume *versus* molality for CMD in water. Degree of substitution: (A) 0.20, (B) 0.73, (C) 1.03, (D) 1.80 and (E) 2.08

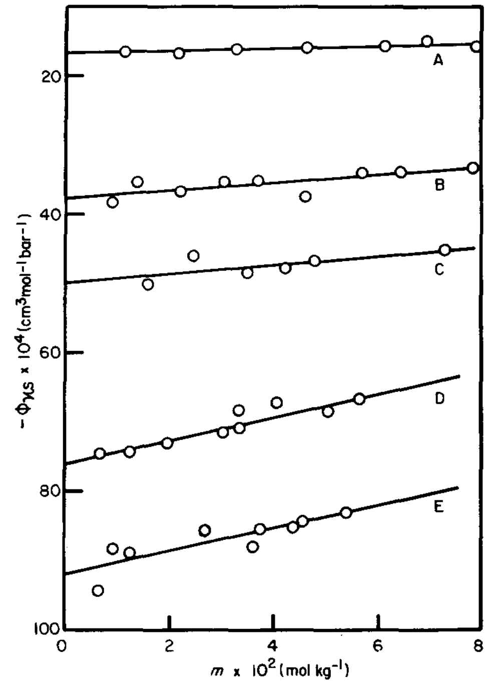

Figure 2 Plots of apparent molar adiabatic compressibility *versus* molality for CMD in water. Degree of substitution: (A) 0.20, (B) 0.73, (C) 1.03, (D) 1.80 and (E) 2.08

The adiabatic compressibility of the solution, β_s (bar^{-1}), was obtained from the data of the sound velocity and density of the solution by the following 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 apparent molar volume, ϕ_v, and apparent molar adiabatic compressibility, ϕ_{KS}, can be represented by the following equations:

$$\phi_v = 1000(d_0 - d)/m d_0 d + M_w/d \qquad (2)$$

and

$$\phi_{KS} = 1000(\beta_s - \beta_{s_0})/m d_0 + \beta_s \phi_v \qquad (3)$$

where m is the molality and M_w the molecular weight of the repeating unit. The subscript '0' refers to the solvent. The partial molar quantities $\bar{\phi}_v$ and $\bar{\phi}_{KS}$ can be obtained from the values of the apparent molar quantities at infinite dilution.

The hydration number of a solute can be estimated from the relation,

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

where $\bar{\phi}_{KS}(h)$ is the partial molar adiabatic compressibility of a hydrated solute, $\bar{\phi}_{KS}(d)$ 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. The value of β_h is assumed to be equal to that of ice, i.e. $\beta_h = 11.1 \times 10^{-6}$(bar^{-1})[14].

RESULTS

Typical experimental results of apparent molar volume and adiabatic compressibility are shown in *Figures 1* and *2*, respectively. The plots of ϕ_v and ϕ_{KS} vs. m were fitted to the linear equation of m by the least mean squares method. The values at $m = 0$ can be regarded as the partial molar quantities. The results of $\bar{\phi}_v$ and $\bar{\phi}_{KS}$ thus obtained for CMC and CMD are summarized in *Tables 1–4*.

In *Figure 3*, the partial molar volumes of CMC and CMD in aqueous solution are plotted against the degree of substitution (*DS*), that is, the average number of $-CH_2COONa$ groups per glucose unit. The plots of $\bar{\phi}_v$ vs. *DS* show straight lines for CMC and CMD, respectively. Similar results for CMD were obtained earlier by Gekko

Table 1 Partial molar volume of CMC (cm^3 mol^{-1})

EtOH (wt%)	Degree of substitution				
	0.56	0.92	1.51	2.04	2.85
0	107.8	117.0	130.2	147.2	168.0
20	111.1	124.8	138.7	144.8	174.5
30	108.7	120.0		158.6	179.4
35			151.5		
40		123.0			177.0
42			146.1		

Table 2 Partial molar volume of CMD (cm^3 mol^{-1})

EtOH (wt%)	Degree of substitution					
	0[a]	0.2	0.73	1.03	1.80	2.08
0	99.1	102.7	118.1	126.1	148.2	154.1
10				125.9	150.5	
20				125.9	148.7	
30				133.8	156.9	
40				129.8	160.5	

[a] Reference 8

Table 3 Partial molar adiabatic compressibility of CMC ($10^{-4}\,\mathrm{cm^3\,mol^{-1}\,bar^{-1}}$)

EtOH (wt%)	Degree of substitution 0.56	0.92	1.52	2.04	2.85
0	−39.0	−59.0	−77.6	−93.8	−118.5
20	−19.5	−20.5	−33.9	−47.0	−67.2
30	−10.3	−12.0		−9.8	−23.5
35			+3.1		
40		+6.7			(+17.0)
42			(+21.6)		

Table 4 Partial molar adiabatic compressibility of CMD ($10^{-4}\,\mathrm{cm^3\,mol^{-1}\,bar^{-1}}$)

EtOH (wt%)	Degree of substitution 0[a]	0.2	0.73	1.03	1.80	2.18
0	−5.7	−16.9	−32.8	−50.1	−76.1	−91.8
10				−42.6	−62.8	
20				−22.9	−41.5	
30				−12.1	−20.0	
40				+4.3	+4.1	

[a] Reference 8

and Noguchi[7]. Linear relationships observed in *Figure 3* are represented by the following equations

$$\bar{\phi}_{\mathrm{v}} = 92.4 + 26.5DS \qquad \text{for CMC} \qquad (5)$$

and

$$\bar{\phi}_{\mathrm{v}} = 99.1 + 26.0DS \qquad \text{for CMD} \qquad (6)$$

The partial molar volume of CMD at $DS = 0$, that is dextran, was obtained by Nomura *et al.*[8] and the intercept in *Figure 3* for CMC gives the partial molar volume of the hypothetical cellulose unit dissolved in water. The partial molar volume of cellulose obtained here is in good agreement with the value ($93\,\mathrm{cm^3\,mol^{-1}}$) estimated by Zana and Tondre[15,16]. They estimated the partial molar volume of cellulose by extrapolating the $\bar{\phi}_{\mathrm{v}}$ values for CMC in the acid form and tetramethylammonium CMC, to zero substitution degree.

Figure 4 shows the partial molar adiabatic compressibilities of CMC and CMD in aqueous solution as a function of DS. The linear relationship between $\bar{\phi}_{\mathrm{KS}}$ and DS is observed for both CMC and CMD, as follows

$$\bar{\phi}_{\mathrm{KS}} = -22.2 - 35.9DS \qquad \text{for CMC} \qquad (7)$$

and

$$\bar{\phi}_{\mathrm{KS}} = -5.7 - 39.7DS \qquad \text{for CMD} \qquad (8)$$

The intercept in equation (7) corresponds to the partial molar adiabatic compressibility of the repeating unit of the hypothetically dissolved cellulose. The value for the hypothetical cellulose is larger than that of dextran. The differences in compressibility are observed for CMC and CMD with the same degree of substitution.

Figures 5 and *6* show respectively the partial molar adiabatic compressibilities of CMC and CMD as a function of ethanol content. The contribution of the adiabatic compressibility of CMC and CMD is the sum of the adiabatic compressibility of the hydration layer and that of the solute itself. When ethanol is added to the aqueous solution of CMC or CMD, water molecules around these solutes are substituted successively by ethanol and are released fully near the precipitation point. Thus, the partial molar adiabatic compressibility just before the precipitation point gives that of the solute in the dehydrated state, that is, the solute itself. The data of the partial molar adiabatic compressibility of CMC and CMD above 40 wt% of ethanol seem to approach the value of dextran, for which the nearly constant value is observed for solvent containing more than 20 wt% of ethanol. The contribution of the $-CH_2COONa$ group to the partial molar adiabatic compressibilities of CMC and CMD in the dehydrated state is negligibly small, since Na^+ and the $-CH_2COO^-$ group are assumed to be incompressible. Therefore, it is reasonable to consider that the partial molar adiabatic compressibility of CMC

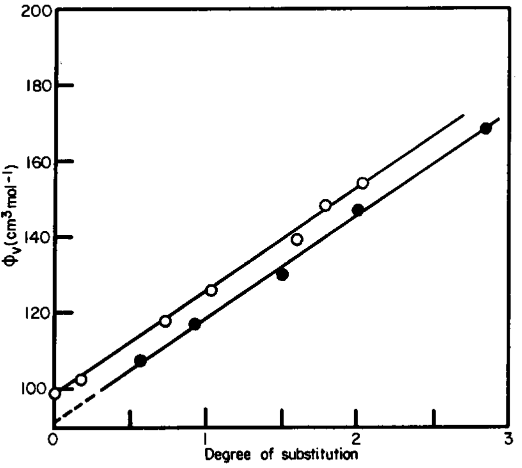

Figure 3 Partial molar volume in water as a function of the degree of substitution. (●) CMC and (○) CMD

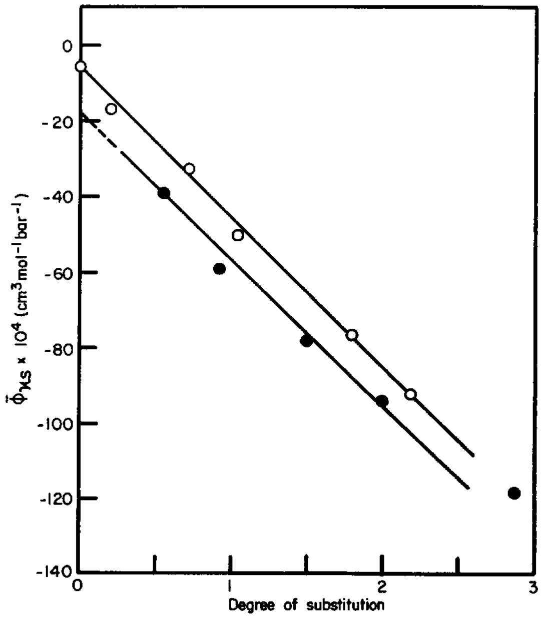

Figure 4 Partial molar adiabatic compressibility in water as a function of the degree of substitution. (●) CMC and (○) CMD

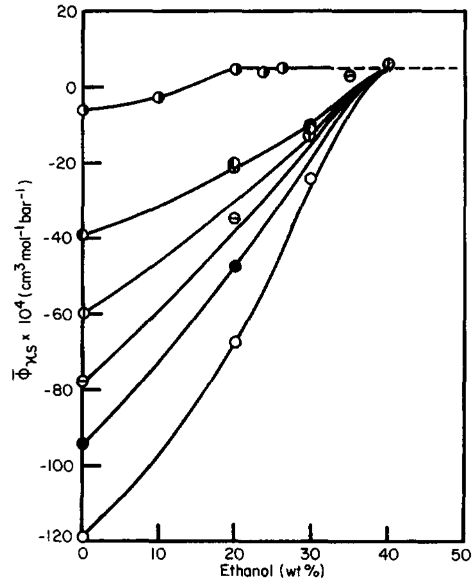

Figure 5 Variation of partial molar adiabatic compressibility of CMC with ethanol content. Degree of substitution: (◑) 0, (◐) 0.56, (⦶) 0.92, (⊖) 1.51, (●) 2.04 and (○) 2.85

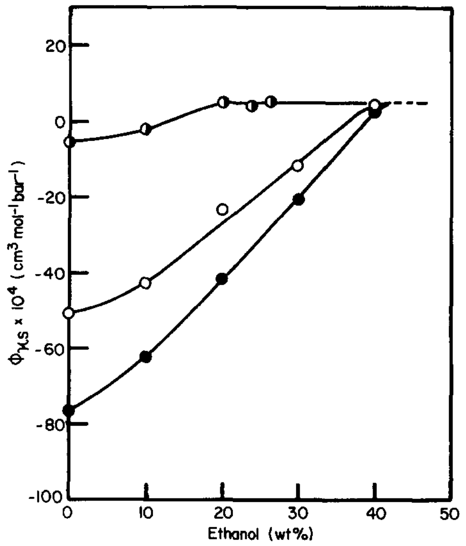

Figure 6 Variation of partial molar adiabatic compressibility of CMC with ethanol content. Degree of substitution: (◑) 0, (○) 1.03 and (●) 1.80

and CMD in the dehydrated state is equal to the value of dextran itself.

The hydration number estimated from equation (4) is shown in *Figure* 7, where $\phi_{KS}(d) = 5.1 \times 10^{-4}\,cm^3\,mol^{-1}\,bar^{-1}$ (ref. 8) is used. As expected from the data of the partial molar adiabatic compressibility above, the hydration numbers of CMC and CMD change linearly with the degree of substitution. Their relationships are represented as

$$n_h = 3.4 + 6.6DS \quad \text{for CMC} \qquad (9)$$

and

$$n_h = 1.8 + 6.7DS \quad \text{for CMD} \qquad (10)$$

These equations indicate that the increment of hydration number with *DS* is similar for CMC and CMD. In other words, the amount of hydration of CMC and CMD increases as a result of the increments of CH_2COONa groups, particularly the Na^+ ion. The hydration layers around CMC and CMD are composed of those of the $-CH_2COONa$ group and those inherent to cellulose and dextran structures.

DISCUSSION

Partial molar volume and adiabatic compressibility

The partial molar volumes of CMC and CMD change linearly with *DS* and their slopes of the plot of ϕ_v vs. *DS* for CMC and CMD are almost the same, as indicated in equations (5) and (6). The increments of the partial molar volume per $-CH_2COONa$ group are $26.5\,cm^3\,mol^{-1}$ for CMC and $26.0\,cm^3\,mol^{-1}$ for CMD. These values are smaller than the partial molar volume of CH_3COONa in water ($\phi_v = 39.75\,cm^3\,mol^{-1}$)[17]. This in fact can be interpreted in terms of the difference in contribution of the $-CH_3$ and $-CH_2$ groups to the partial molar volume. Several studies have been carried out in order to estimate the group contribution and similar results have been obtained. Harada *et al.* indicated that the group contributions of $-CH_3$ and $-CH_2$ are 26.4 and $15.9\,cm^3\,mol^{-1}$ (ref. 18), respectively, estimated from data of ethylene glycol derivatives. The partial molar volume of $-CH_2COONa$ estimated by the substitution of CH_3- in CH_3COONa by $-CH_2$ is $29.5\,cm^3\,mol^{-1}$. This value is in close agreement with those of the increment of the partial molar volume per $-CH_2COONa$. The slight decrease of the group contribution of $-CH_2COONa$ to the partial molar volume may suggest that Na^+ is strongly attracted to COO^-.

There exists a slight difference in the partial molar volume between dextran and hypothetical cellulose. In general, it might be considered that the partial molar volume for β-glucose is larger than that for α-glucose[19–21], since the OH group of β-glucose prefers the axial orientation, while that of α-glucose is in favour of the equatorial position. However, this is not the case in our experimental results. Therefore, the difference in the partial molar volumes is mainly ascribed to the different type of the linkage in the repeating units. In the β-1,4-

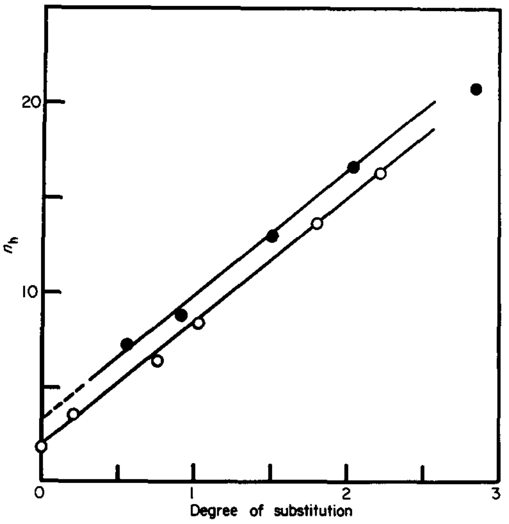

Figure 7 Hydration number (n_h) as a function of the degree of substitution. (●) CMC and (○) CMD

linkage, only one O atom exists between the C1 and C4 atoms. On the other hand, in the α-1,6-linkage, the C1 atom is separated from the C6 atom by the $-CH_2-O-$ group. Consequently, CMD has a larger void space than CMC.

The partial molar volumes of CMC and CMD increase with ethanol content, as listed in *Tables 1* and *2*. The partial molar volume of a polyelectrolyte, such as CMC and CMD, may be written as[7,22,23]

$$\bar{\phi}_v = \bar{\phi}_p + \bar{\phi}_c \tag{7}$$

and

$$\bar{\phi}_p = \bar{\phi}_{p,int} + E_p + H_p \tag{8}$$

where $\bar{\phi}_p$ and $\bar{\phi}_c$ are the partial molar volumes of the polyion and counterion, respectively, $\bar{\phi}_{p,int}$ the intrinsic ionic volume, E_p the contribution from the electrostriction of hydrated water and H_p from the hydrophobic contribution. The value of $\bar{\phi}_c$ for Na^+ decreases with ethanol content. Therefore, the increase of $\bar{\phi}_v$ for CMC and CMD is due to the change of $\bar{\phi}_p$. Since the intrinsic volume of ions is not affected by the change of the composition of water–ethanol mixtures, the terms of E_p and H_p should change with the ethanol content. Nomura *et al.* indicated that the partial molar volume of dextran in water–ethanol mixtures is independent of the composition of the ethanol–water mixtures. Similar results were obtained for α-, β- and γ-cyclodextrins[24]. These results imply that the hydrophobic term, H_p, is almost independent of the ethanol content. Thus, the main factor for the increase of the partial molar volume with ethanol content is the decrease of relaxation of the electrostriction around $-CH_2COO^-$.

Similar to the case of the partial molar volume, the partial molar adiabatic compressibility of CMC per $-CH_2COONa$ is approximately consistent with that of CMD. The contribution of $-CH_2COONa$ to $\bar{\phi}_{KS}$ is -35.9 and $-39.7 \times 10^{-4}\,cm^3\,mol^{-1}\,bar^{-1}$ for CMC and CMD, respectively. It is well known that the contribution of $-CH_2COO^-$ to $\bar{\phi}_{KS}$ is very small in comparison with that of Na^+. The ionic partial molar adiabatic compressibility of Na^+ depends on the manner of division of this quantity. In general, the value for Na^+ lies at -32×10^{-4} to $-38 \times 10^{-4}\,cm^3\,mol^{-1}\,bar^{-1}$ (ref. 25). In addition, the group contribution of $-CH_2COONa$ estimated from $CH_3(CH_2)_4CH_2COONa$[26] is $-38.3 \times 10^{-4}\,cm^3\,mol^{-1}\,bar^{-1}$, where the group contribution of CH_3- and $-CH_2$ to ϕ_{KS} are 1.3×10^{-4} and $-1.8 \times 10^{-4}\,cm^3\,mol^{-1}\,bar^{-1}$ (ref. 18), respectively. Therefore, ϕ_{KS} for CMC and CMD changes with the amount of Na^+ in a glucose unit.

Hydration of CMC and CMD

The hydration number of CMC is larger than that of CMD, but their partial molar volumes show the inverse relation. It is assumed that equatorial OH groups are more extensively hydrated in water than axial ones[19–21]. Therefore, the cellulose bonded by the β-1,4-linkage hydrates water molecules more than α-1,6-linked dextran. When a proton in the OH group is substituted by a $-CH_2COONa$ group, the hydration number inherent to cellulose or dextran structure remains unchanged. Consequently, the increment of hydration number of CMC and CMD with *DS* is interpreted in terms of the increase of the amount of the hydration of $-CH_2COONa$.

Gekko and Noguchi investigated the molecular weight dependence of the hydration for oligodextran[7]. They indicated that the amount of hydration of oligodextran depends on the conformation but is almost independent of the molecular weight above *ca.* 2000. The conformation of polyion changes with the charge density, which in turn varies with *DS* or the degree of neutralization. The additivity of the hydration of CMC and CMD holds well with regard to *DS*. This fact means that the hydration of the polyion investigated here is almost independent of the change of conformation of polyion. Thus, the hydration behaviour of CMC and CMD is determined by the local structure of these materials. Moreover, no specific hydration layer is created by the action of the strong electric field due to polyion.

ACKNOWLEDGEMENT

The authors wish to thank Daicel Chem. Ind. for supplying them carboxymethyl cellulose samples.

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