Viscosity of Aqueous Solutions of Polysaccharides and Their Carboxylate Derivatives

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Synopsis

The viscosities of aqueous solutions of methyl cellulose, dextran, and their carboxymethyl derivatives were measured as functions of molecular weight and concentration. Furthermore, effects of ionic group and added salt on the viscosity of aqueous solutions of carboxymethyl derivatives were investigated. The viscosities of dextran and carboxymethyl dextran solutions did not show any shear stress dependence, but those of methyl and carboxymethyl cellulose solutions strongly depended on shear stress even at low concentrations. The results were discussed on the basis of the points of molecular structure and hydration and ionic interaction of a polymer chain in solutions.

INTRODUCTION

Increasing the concentration of polymer solutions, motions of polymer chains are strongly influenced by polymer–polymer intermolecular interactions. These interactions mainly determine the shear rate dependence of the viscosity of the polymer solutions. However, other factors, such as the local molecular structure, the type of linkage of the polymer chain, and the specific interactions between polymer and solvent, are also needed to understand the flow properties of polymer solutions.

The viscosities of aqueous solutions of methyl cellulose and polyacrylic acid show the strong shear rate dependence even in the low concentration ranges. These materials have a number of hydrophobic or ionic groups in a chain and these groups strongly affect their solution properties. In order to know how the flow properties are related to short range interactions such as hydration and hydrophobic interaction, as well as long range ion–ion interaction, the polysaccharides are very suitable materials, because the samples with different ratios of the hydrophilic and hydrophobic groups are available and also the flow properties of polysaccharide derivatives depend on their solubility in water.

For example, dextran and cellulose show quite different properties, that is, the former is highly soluble in water, but the latter is insoluble. However, the glucose is a common structure unit of dextran and cellulose and only the difference between them is a type of linkage, that is, dextran links D-glucose with the α-1,6 glucoside linkage and cellulose with the β-1,4 linkage. Besides, D-

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glucose is very soluble in water and its concentrated solutions show the flow properties of typical supercooled liquids at very low temperatures. If the OH groups in cellulose are substituted by OCH_3 groups, it is transformed into methyl cellulose which is water-soluble, because the substitution of OH groups on cellulose with OCH_3 groups prevents the cellulose from recrystallizing. In aqueous solutions, OCH_3 groups act as hydrophobic sites. The OH groups in dextran and cellulose can also be substituted by $OCH_2 COONa$, carboxymethyl groups, which changes them to polyelectrolytes.

Rheological properties of cellulose and/or dextran derivatives in dilute solution have been investigated by many workers.[1-7] However, papers referring to the concentration or shear dependences of viscosities of these materials are few.[8-10] In this paper, in order to elucidate the effects of the hydration and ionic interaction on the flow properties of polymer solutions at moderate concentrations, the viscosity measurements of aqueous solutions of polysaccharides and their carboxylate derivatives were carried out systematically as functions of shear stress, concentration, molecular weight, and degree of substitution of carboxymethyl group.

EXPERIMENTAL

Samples

Methyl cellulose (MC) samples used were purchased from Nakarai Chemicals, Co. Ltd. and dextrans (DX) from Pharmacia Fine Chemicals (Sweden). Their molecular weights range from 1.33×10^4 to 1.14×10^5 for methyl cellulose and from 10^4 to 2×10^6 for dextran. For MC, the content of the methoxy group was 28.5%. Carboxymethyl celluloses (CMC) were kindly supplied from Daisel Chemical Industries Ltd. Carboxymethyl dextran (CMD) samples were prepared by esterification of dextran with NaOH and reaction with monochloroacetic acid.[11] After purification, the degree of substitution (DS) of the carboxymethyl group was determined by titration method. The molecular weight and degree of substitution of the carboxymethyl group of the samples used are summarized in Table I.

Measurements

The viscosity measurements were carried out by means of the capillary viscometer of Maron–Krieger–Sisko type.[12] A diagram of Maron–Krieger–Sisko

TABLE I
Molecular Weight and Degree of Substitution (DS) of the Carboxymethyl Cellulose (CMC)
and Carboxymethyl Dextran (CMD) Samples

CMC		CMD	
M_w	DS	M_w	DS
49,000	0.56	45,000	0.26
52,000	0.92	60,000	1.03
65,000	1.51	64,000	1.20
1–20,000	2.85	72,000	1.60
		76,000	1.80
		83,000	2.20

type viscometer used is shown in Figure 1. The apparatus made entirely of Pyrex glass consists of a capillary unit (I) and a manometer unit (II) connected by a ball and socket joint E. The capillary units are composed of a capillary and water jacket as shown in Figure 1. Capillary units with two different capillary sizes (2.52 and 4.96 mm in diameter) were used. The shear stress was changed from 5 to 200 g/cm s^2, using the water and mercury drive methods.

The concentration range of the aqueous solutions of each sample was from 0.5 to 30 wt % and the measurements were carried out at 25°C. For each sample solution, the viscosity measurements were done as functions of shear stress, concentration, molecular weight, and degree of substitution of carboxyl groups.

RESULTS AND DISCUSSION

Viscosity in Dilute Solutions

The intrinsic viscosity is defined as

$$[\eta] = \lim_{C \to 0} \frac{\eta - \eta_0}{\eta_0} \frac{1}{C} \tag{1}$$
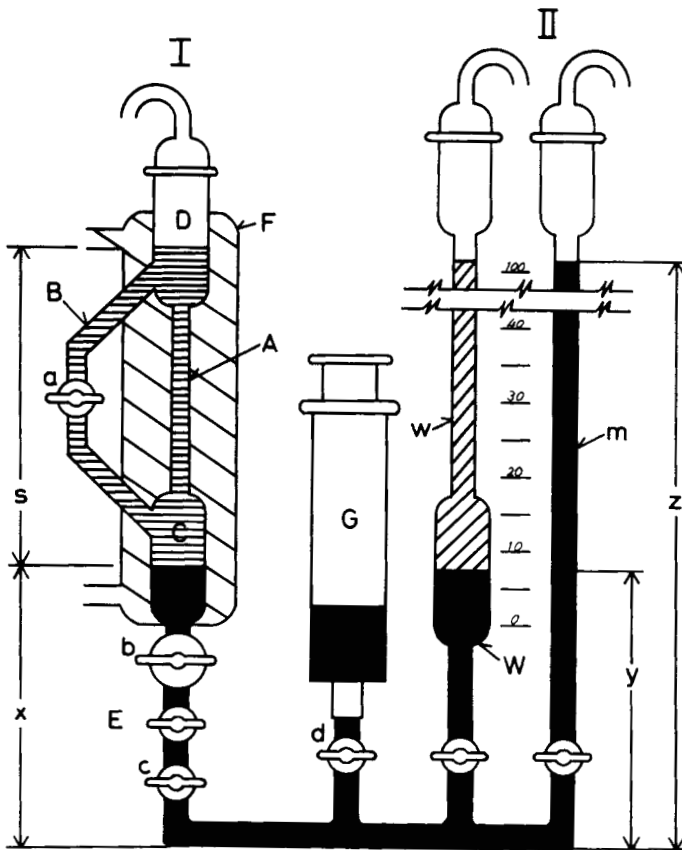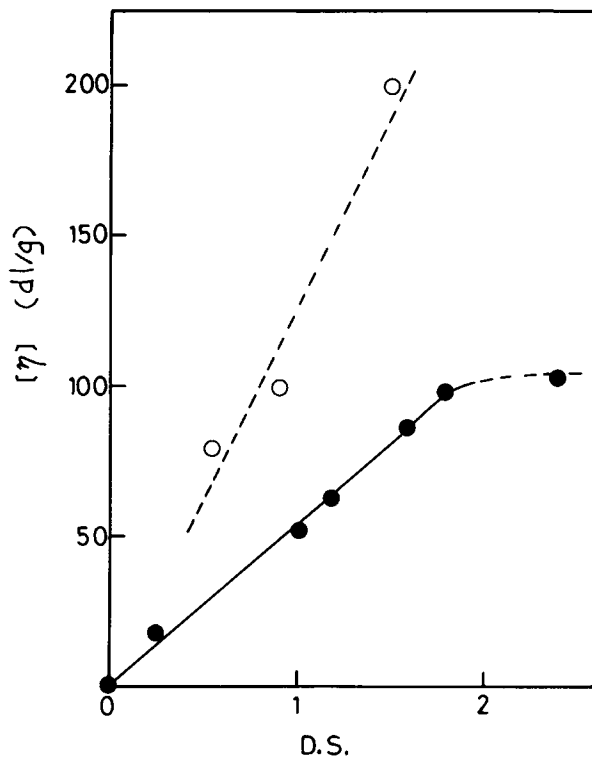

Fig. 1. Block diagram of MSK viscometer.

Fig. 2. Intrinsic viscosity [η] as a function of degree of substitution, DS: (○) CMC; (●) CMD.
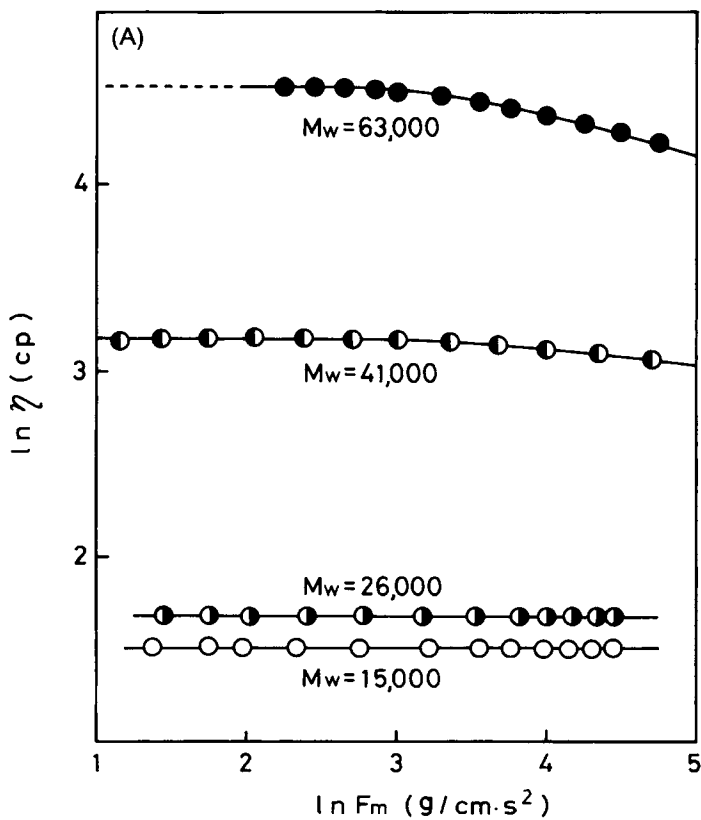

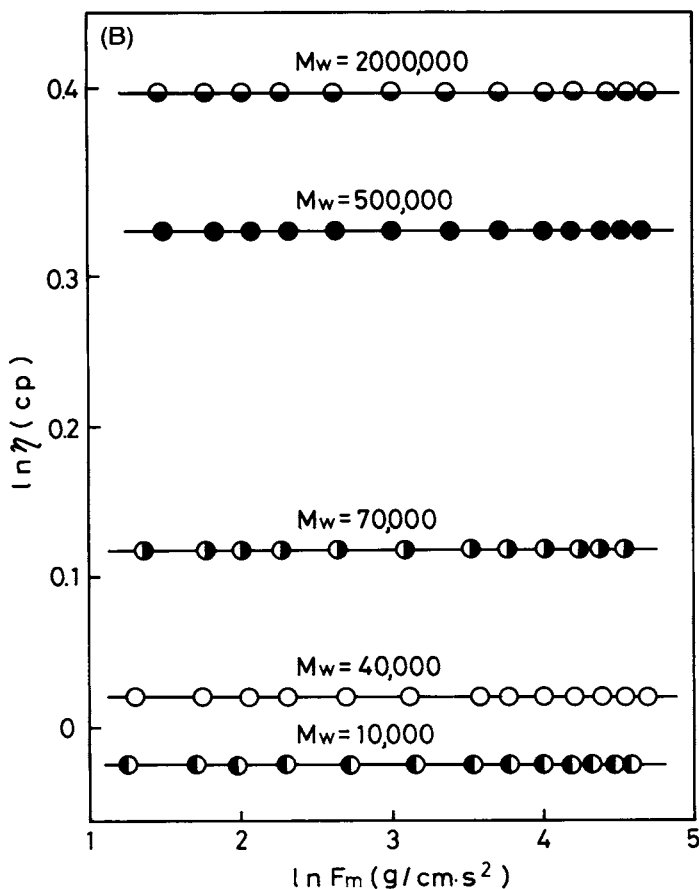Fig. 3. Molecular weight dependence of flow curves; concn = 1 wt %: (A) MC; (B) DX.

Fig. 3 (*Continued from the previous page*)

which is related to the molecular weight as $[\eta] = KM_t^a$. The parameter a works as a very useful measure representing the state of polymer chains in solution. For aqueous solutions of MC and DX, the relationships between $[\eta]$ and M_t are found in the literature as[1,5]

$$MC: \quad [\eta] = 3.16 \times 10^{-3} M_t^{0.55} \qquad (2)$$

$$DX: \quad [\eta] = 9.78 \times 10^{-4} M_t^{0.5} \qquad (3)$$

The parameter a ranges from 0.5 to 0.55 for both MC and DX in aqueous solutions. These values of a clearly indicate that the polymer chains in MC and DX are both in Gaussian coil state at finite dilute concentrations in solution.

For the polyelectrolytes in aqueous solutions with added salts, the relationship between $[\eta]$ and the degree of polymerization can be also empirically expressed as[13]

$$NaCMC: \quad [\eta] = 16.6 K_m P \ (0.1 \ M \ NaCl) \qquad (4)$$

$$NaCMD: \quad [\eta] = K'_m P \ (0.1 \ M \ NaCl) \qquad (5)$$

where K_m and K'_m are both functions of degree of substitution. The reported factors of a for aqueous solutions of cellulose nitrate and NaCMC range from 0.8 to 1.0.[14] This figure shows that these polyelectrolyte chains in dilute solutions containing NaCl are in more extended states than the case of the MC and DX chains.

The intrinsic viscosity $[\eta]$ of polyelectrolytes in aqueous solutions without added salts can be expressed by the Fuoss equation[15]

$$[\eta] = \lim_{C \to 0} \frac{A}{B + \sqrt{C}} + D \qquad (6)$$

Figure 2 shows the relationship between $[\eta]$ and DS, for the samples CMC and CMD in aqueous solutions without salts. The values of $[\eta]$ of CMD and CMC increase with increasing degree of substitution, that is, the number of $-OCH_2COONa$ groups per glucose unit. The main cause in the change of the intrinsic viscosity is ascribed to the conformational change of the main chain due to the electrostatic interactions between the charged groups.
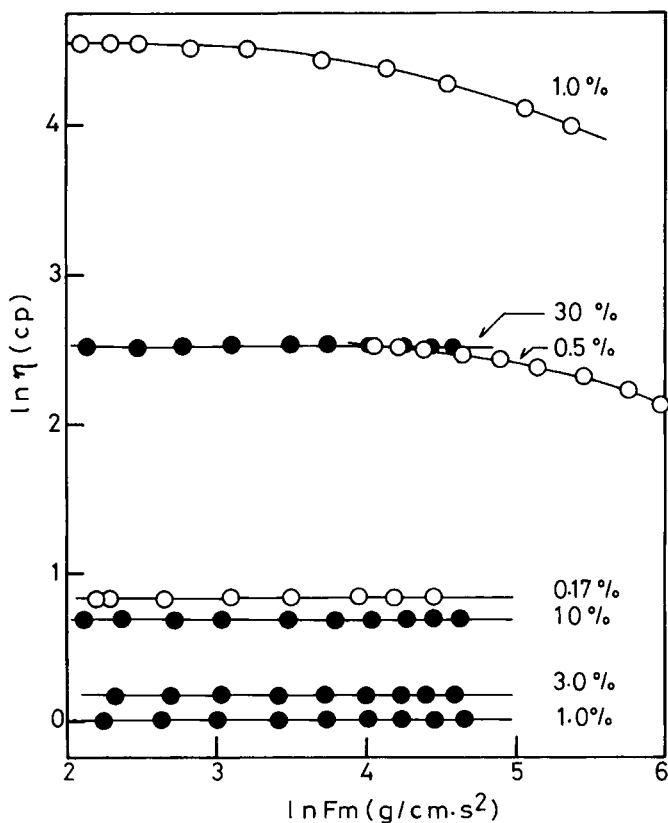

Fig. 4.   Concentration dependence of flow curves for MC (○) and DX (●). M_w(MC) = 6.3 × 10⁴; M_w(DX) = 4 × 10⁴.

In a previous paper,[16] we found that the partial molar volumes and compressibilities of CMC and CMD increase linearly with increasing degree of substitution. It was indicated there[16] that the difference in the hydration for CMC and CMD is small and the incremental amount of hydration with the degree of substitution is ascribed to the introduction of the OCH_2COONa group to glucose unit. However, the large difference in intrinsic viscosity between CMC and CMD could not be interpreted only in terms of the change of the chemical structure arising from the introduction of OCH_2COONa groups.

It is well known that dextran is typical branched polymer and the intrinsic viscosity of a branched polymer is lower than that of a linear one at the same molecular weight. The effect of branching on the intrinsic viscosity can be estimated by the ratio g of unperturbed mean square radii of randomly branched and unbranched molecules having the same chemical constitution and molecular weight. We determined the g value of dextran used ($M_w = 4 \times 10^4$) as 0.8–0.9 from the interpolation of Senti's result.[1] As CMD samples are prepared from the dextran of molecular weight 4×10^4, the g value of CMD will be the same as DX. The intrinsic viscosity of CMD will increase about 20–40% if there is
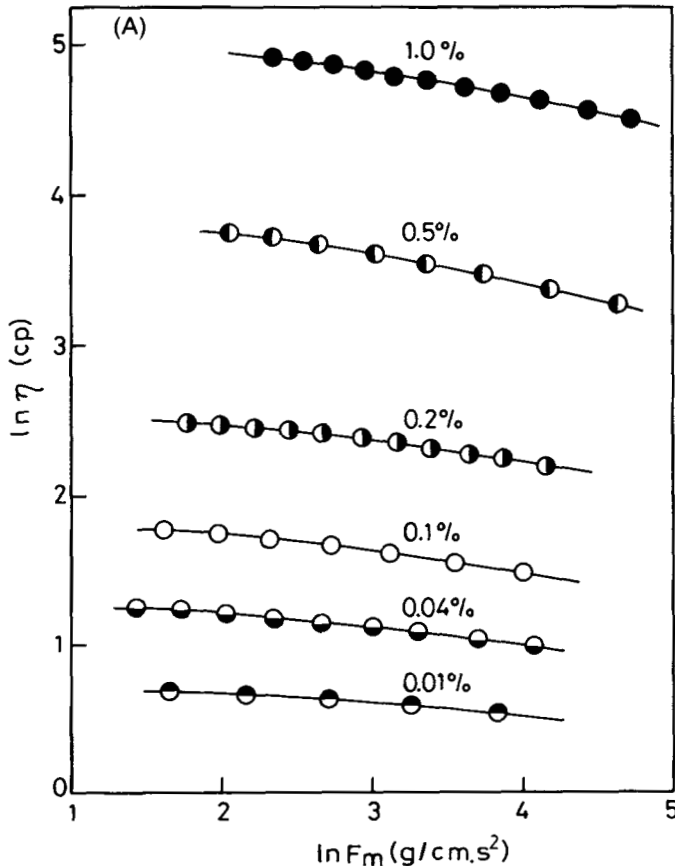

Fig. 5. Concentration dependence of flow curves (A) for CMC and (B) for CMD. M_w(CMC) $= 6.5 \times 10^4$, DS $= 1.5$; M_w(CMD) $= 6.4 \times 10^4$, DS $= 1.2$.
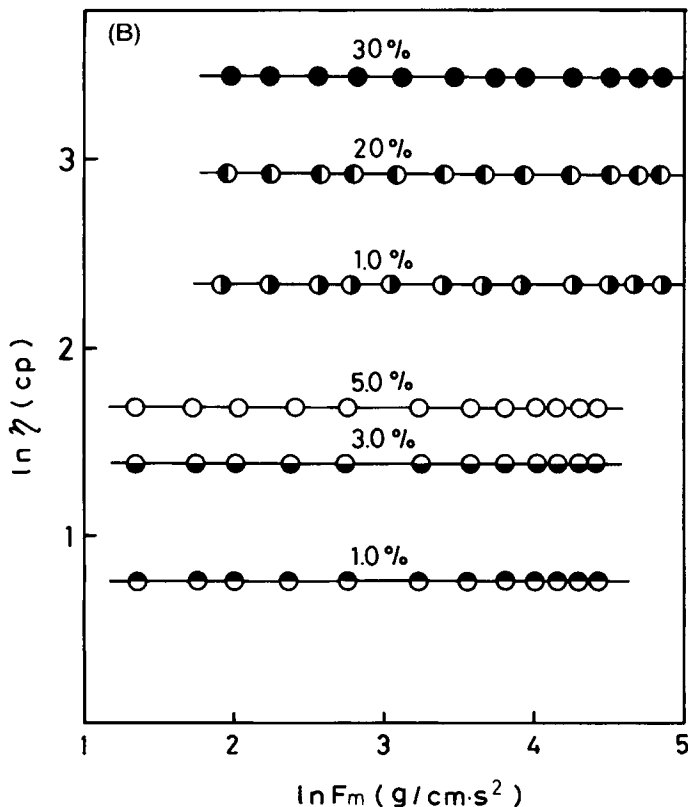
Fig. 5 (*Continued from the previous page*)

no branching. The difference of intrinsic viscosity between CMC and CMD can be partly explained by the branching effect. CMD is constituted of the α-1,6-linking glucose unit and it is separated by $-CH_2-O-$ and the OH or OCH_2COONa groups prefer the equatorial orientation. Therefore, the repulsive force of CMD is weaker in comparison with that of CMC. This may be alternative effect to reduce the intrinsic viscosity of CMD.

Molecular Weight Dependences (MC and DX)

The molecular weight dependences of viscosity of MC and DX are shown in Figures 3 (A) and (B). The shear rate dependences of the viscosity of MC solutions show the non-Newtonian behavior above $M_w = 4 \times 10^4$ at the concentration of 1 wt %. DX samples at the same concentration, however, show Newtonian flow up to $M_w = 2 \times 10^6$ investigated here. The values of η of MC solutions are much larger than those of DX at the similar molecular weights and concentrations, as expected from the dilute solution properties.

Concentration Dependences

(i) MC and DX: MC solutions show the non-Newtonian flow at the very low concentration, but no shear stress dependence was observed for DX solu-
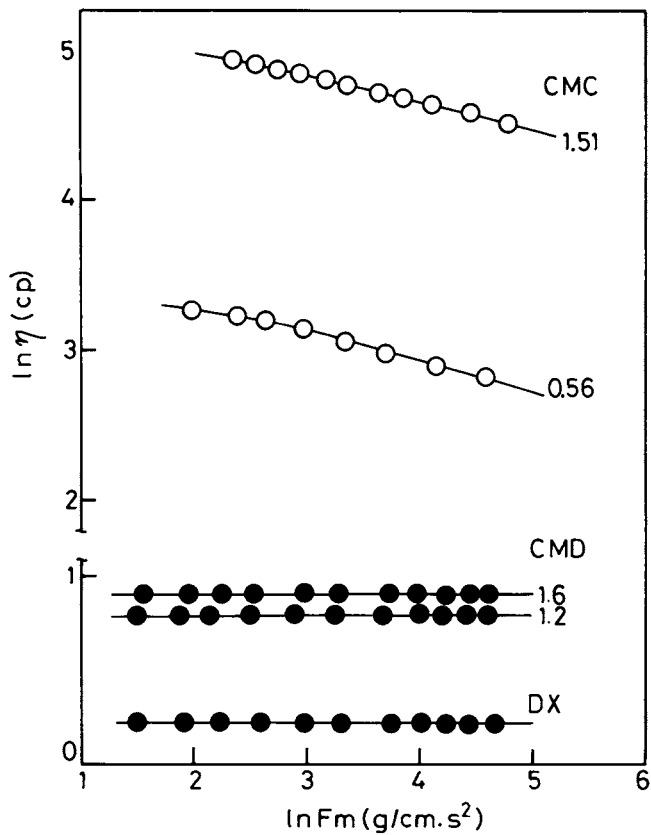
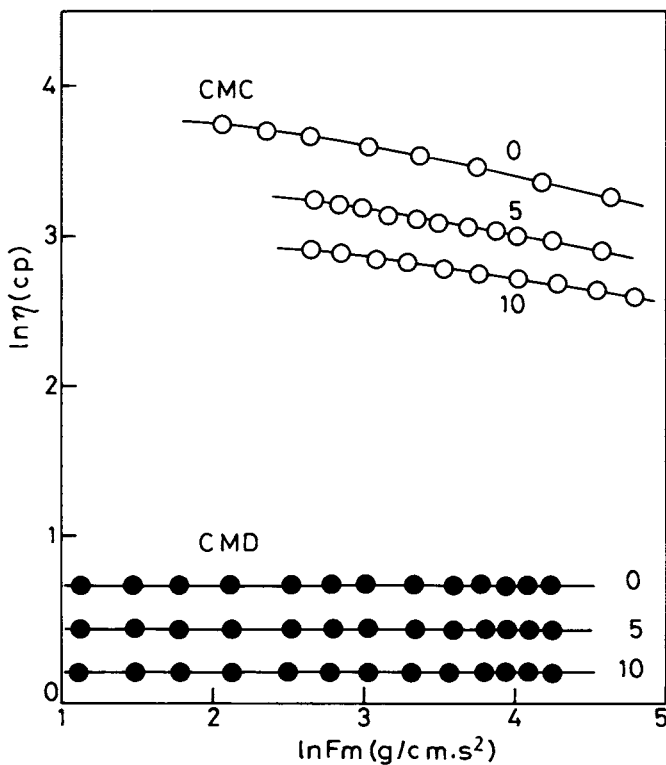Fig. 6. Effect of DS on flow curves: (○) CMC; (●) CMD; concn = 1 wt %.

Fig. 7. Effect of added NaCl on flow curves. concn = 1 wt %, M_w(CMC) = 6.5 × 10^4, DS = 1.5; M_w(CMD) = 6.4 × 10^4, DS = 1.6. The values of $C_{NaCl/Cp}$ are given in the figure.
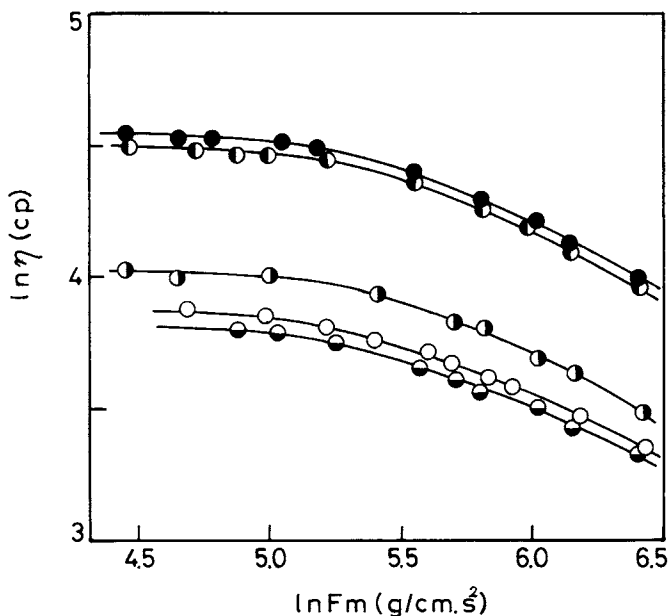
Fig. 8.   Effect of added NaCl on flow curves for the highest charged density CMC, DS = 2.85.
concn = 1.0 wt%; $C_{NaCl/Cp}$ = 0 (●), 0.1 (◐), 1 (◑), 5 (○), and 10 (◒).

tions at any concentration and shear stress ranges investigated here, as shown
in Figure 4.

(ii) CMC and CMD: In the case of CMD, the increase of concentration did
not affect the shear stress dependence. On the contrary, with increasing con-
centration, the strong shear stress dependence for CMC solutions was observed
as shown in Figure 5.

Effects of Ionic Groups

The effects of the ionic group, COO^-, on the flow properties of CMC and
CMD are quite similar. The increase of the ionic groups in a polymer chain
increases the non-Newtonian effects of flow curves for CMC, but has little
effect on the original flow properties of MC and DX solutions (see Fig. 6).

Effects of Added NaCl

With addition of NaCl, the electrostatic field around polyions was shielded
and the ionic interaction was weakened. As expected, the addition of NaCl to
CMC and CMD solutions reduces the viscosity of solutions (see Figs. 7 and
8). This effect corresponds to that in decreasing the amount of the ionic groups
in a polymer chain. The apparent viscosities of CMC and CMD in aqueous
solutions containing NaCl are estimated from Figures 7 and 8 and their results
are summarized in Table II. The apparent viscosity of the CMC sample for the
highest charge density decreased sharply with increasing added salt, NaCl. The
apparent viscosities of all samples at the concentration of NaCl, of $C_{NaCl}/$
$C_{CMCorCMD}$ = 10, were reduced to half of the values for salt-free solutions. This
fact clearly indicates that the local structure of samples also plays very important

TABLE II
Apparent Viscosities of CMC and CMD in Aqueous Solution Containing NaCl
with Various C_{NaCl}/C_p, Where C_p is the Concentration of CMC or CMD

C_{NaCl}/C_p	CMD (DS = 1.60)	CMC (DS = 1.51)[a]	CMC (DS = 2.85)[b]
0	1.93	38.5	100
0.1			87.3
1			54.7
5	1.31	25.0	46.6
10	1.06	18.2	43.1

[a] The values are estimated at $\ln F_m = 2.75$ in Figure 7.
[b] The values are estimated at $\ln F_m = 4.75$ in Figure 8.

role in the flow properties of polymer solutes in solutions, as well as the expansion state of polymer chains arising from the ionic repulsive force.

CONCLUSION

The viscosities of solutions of DX and CMD did not show any shear stress dependence, whereas those of MC and CMC show a strong shear stress dependence. Besides, the viscosities of the latter samples are much larger than those of the former. The different flow properties in dextran and cellulose derivatives can be interpreted by only the effects of the substitution of OH groups by the OCH_3 or OCH_2COONa groups and their hydration nature. The non-Newtonian flow properties of MC and CMC are mainly due to the original chemical structure, that is the β-1,4 linkage.

References

1. F. R. Senti, N. N. Hellman, N. H. Ludwig, G. E. Babcock, R. Tobin, C. A. Glass, and B. L. Lamberts, *J. Polym. Sci.*, **27**, 527–546 (1955).

2. K. A. Granath, *J. Colloid. Sci.*, **13**, 308–328 (1958).

3. W. R. Moore and A. M. Brown, *J. Colloid. Sci.*, **14**(1), 343–353 (1959).

4. V. K. Uda and G. Meyerhoff, *Macromol. Chem.*, **47**, 168–184 (1961).

5. W. B. Neely, *J. Polym. Sci. A*, **1**, 311–320 (1963).

6. E. Riande and J. M. Perena, *Makromol.*, **175**, 2923–2938 (1974).

7. J. H. Elliot and Gantz, *Rheol. Acta*, **13**, 670 (1974).

8. H. Elmgren, *Biopolymers*, **23**, 2525–2541 (1984).

9. K. Mashiko and T. Matsumoto, *Nihon Reoroji Gakkaishi*, **14**, 93–98 (1986).

10. B. Ernst, P. Navard, and J. M. Haudin, *J. Polym. Sci. B*, **26**, 211–219 (1988).

11. K. Gekko and H. Noguchi, *Biopolymers*, **14**, 2555–2565 (1975).

12. S. H. Maron, I. M. Krieger, and S. W. Sisko, *J. Appl. Phys.*, **25**, 971–976 (1954).

13. M. Ichiba, Bachelor thesis, Nagoya University, 1966, p. 5.

14. M. L. Huggins, *Cellulose and Cellulose Derivatives*, E. Ott, H. H. Spurlim, and M. W. Grafflin, Eds., Wiley-Interscience, New York, 1955, p. 1195.

15. R. M. Fuoss and U. P. Strauss, *J. Polym. Sci.*, **3**, 246 (1948).

16. S. Koda, S. Hasegawa, M. Mikuriya, F. Kawaizumi, and H. Nomura, *Polymer*, **29**, 2100 (1988).