

The Non-Newtonian Viscosity of Dilute Aqueous Solution of Methylcellulose

Naomichi Iso and Daijiro YAMAMOTO

Faculty of Agriculture, Meiji University, Ikuta, Kawasaki

(Received October 30, 1967)

The viscometric behavior of a dilute aqueous solution of methylcellulose was studied by tilting capillary viscometers. The intrinsic viscosity was obtained by the extrapolation of Martin's plots on the assumption that the plots were linear down to an infinite dilution. The intrinsic viscosity obtained increased with the rate of shear over the range of 200—1200 sec⁻¹. Huggins' constant, k' , the temperature coefficient of the intrinsic viscosity, $d[\eta]/dT$, and the energy of the activation of flow, E_p , decreased with the rate of shear. From the data of $d[\eta]/dT$ and E_p thus obtained, it has seemed reasonable to assume that the methylcellulose chain has a relatively small flexibility and a strong tendency toward alignment with a flowing stream. This may be the main reason why the viscosity of the dilute aqueous solution of methylcellulose is non-Newtonian.

Methylcellulose is a kind of cellulose-ether used extensively in food products as a thickener, a stabilizer, a swelling agent, a coating agent, a molding agent, and a binder. During the course of an investigation into the viscosity of a concentrated methylcellulose solution,^{1,2)} our attention was called to the viscosity of a dilute solution of the same sample. Although the viscosity of a dilute solution of methylcellulose has been studied by several workers³⁻⁵⁾ in recent years, little attention has been paid to the non-Newtonian viscosity of the dilute solution.

On the other hand, the shear-rate dependence of the intrinsic viscosity of a high polymer solution has been investigated both theoretically and experimentally, and these results have been reviewed by several workers.⁶⁻⁹⁾ Most experiments and theories have found that the intrinsic viscosity decreased with

the shear rate,^{6,10-17)} although theories which do not give a shear-rate dependence of the viscosity have been reported, too.¹⁸⁻¹⁹⁾ Furthermore, a few theories and experiments have shown that the intrinsic viscosity increases with the shear rate in some cases.^{8,20,21)}

The purpose of this study is to extend the investigation of the viscometric behavior of methylcellulose solutions to a low rate of shear and to a low concentration of the solution. The temperatures measured range from 25°C to 45°C, for it is found that a gelation of the solute takes place above about 50°C.²⁾ In that region the energy of the activation of the flow of the solution and the temperature dependence of the intrinsic viscosity have also determined in order to discuss the non-Newtonian viscosity of the solution.

Experimental

Materials. The methylcellulose was a product of Shinetsu Chemical Ind. (trade name, "Metolose 90 SH 15000"). The manufacturer reported that the density was 1.31 g/cm³; the degree of methylation of this sample was 1.08—1.42. The white powder of the sample was dissolved in distilled water without further purification; the concentration of the original solution was 0.3030 g/100 ml.

Viscosity Measurement. Four tilting capillary viscometers²²⁾ were used. Each viscometer was a modification of the dilution suspended-level viscometer. The

1) D. Yamamoto, N. Iso and N. Ikawa, *Bull. Fac. Agr. Meiji Univ.*, **20**, 17 (1966).

2) D. Yamamoto, N. Iso and N. Ikawa, *ibid.*, **21**, 51 (1967).

3) K. Uda and G. Meyerhoff, *Makromol. Chem.*, **47**, 168 (1961).

4) K. Uda, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **82**, 1597 (1961).

5) W. Kuhn, P. Moser and H. Majer, *Helv. chim. Acta*, **44**, 770 (1961).

6) A. Peterlin and M. Cöpic, *J. Appl. Phys.*, **27**, 434 (1956).

7) E. Passaglia, J. T. Yang and N. J. Wegemer, *J. Polymer Sci.*, **47**, 333 (1960).

8) A. Peterlin, *J. Chem. Phys.*, **33**, 1799 (1960).

9) Y. Chikahisa, *Kobunshi (High Polymers, Japan)*, **15**, 228 (1966).

10) R. Cerf, *J. Polymer Sci.*, **23**, 125 (1957).

11) Y. Ikeda, *J. Phys. Soc. Japan*, **12**, 378 (1957).

12) F. Bueche, *J. Chem. Phys.*, **22**, 1570 (1957).

13) T. W. Dewitte, *J. Appl. Phys.*, **26**, 889 (1955).

14) T. Takemura, *J. Polymer Sci.*, **28**, 185 (1958).

15) Y. H. Pao, *ibid.*, **61**, 413 (1962).

16) Y. Chikahisa and T. Fujiki, *J. Phys. Soc. Japan*, **19**, 2188 (1964).

17) N. Yamaguchi, *Sci. Papers I.P.C.R.*, **42**, 1 (1966).

18) P. E. Rouse, *J. Chem. Phys.*, **21**, 1272 (1955).

19) B. H. Zimm, *ibid.*, **24**, 269 (1956).

20) A. Peterlin and D. T. Turner, *ibid.*, **38**, 2315 (1963).

21) S. P. Burow, A. Peterlin and D. T. Turner, *Polymer*, **6**, 35 (1965).

22) E. Wada, *J. Polymer Sci.*, **16**, 305 (1954).

TABLE 1. THE INTRINSIC VISCOSITY, $[\eta]$ (100 ml/g), OF DILUTE AQUEOUS SOLUTION OF METHYLCELLULOSE AND TEMPERATURE COEFFICIENT OF INTRINSIC VISCOSITY, $d[\eta]/dT$

T ($^{\circ}\text{C}$)	$g(F)$ (sec^{-1})						
	0	200	400	600	800	1000	1200
25	11.17	11.39	11.74	10.84	—	—	—
30	9.70	9.93	10.13	10.10	10.22	—	—
35	7.98	8.36	8.24	8.19	8.61	—	—
40	7.02	7.35	7.28	7.10	6.87	7.05	—
45	5.45	5.48	5.54	5.61	5.60	5.68	5.73
$-d[\eta]/dT$	0.28	0.29	0.31	0.30	0.31	—	—

capillaries of these viscometers ranged from 0.34 to 0.84 mm in diameter. Aqueous solutions of sucrose were used for the calibration of the viscometers, for Bingham and Jackson²³⁾ have shown that an aqueous solution of sucrose is suitable for this purpose.

The relative viscosity, η_r , is given by the following equation:¹⁷⁾

$$\eta_r = \left[\frac{4(t_s/t_0)}{3 + (t_s/t_0)(dt_s/dt_0)} \right] \times \left[1 + \frac{(V^2/\pi R^4 g h)(1/t_0^2 - 1/t_s^2)}{1} \right], \quad (1)$$

where V is the total volume flowing in time t , while the suffixes s and 0 denote the solution and the solvent respectively. R is the radius of the capillary, h is the mean head of the liquid, and g is the acceleration due to gravity. The rate of shear at the capillary wall is expressed by:

$$g(F) = 4V/\pi R^3. \quad (2)$$

The intrinsic viscosity, $[\eta]_{g(F)}$, at a constant rate of shear is calculated from Martin's equation:²⁴⁾

$$\log(\eta_{sp}/c) = \log[\eta] + k[\eta]c, \quad (3)$$

where η_{sp} is the specific viscosity, c is the concentration of the solution, and k is a constant.

Results and Discussion

Figure 1 shows an example of the shear-rate dependence of the relative viscosity. As the figure shows, the viscometric behavior of the dilute solution of methylcellulose was non-Newtonian; this non-Newtonian behavior of the solution decreased with a decrease in the concentration of the solution. The values of $\log(\eta_{sp}/c)$ at a constant rate of shear were plotted against the concentration according to Martin's equation. An example of the plots of $\log(\eta_{sp}/c)$ versus c is shown in Fig. 2.

The intrinsic viscosity at a constant rate of shear was obtained by the extrapolation of each plot of $\log(\eta_{sp}/c)$ versus c to an infinite dilution. The values of $[\eta]_{g(F)}$ are shown in Table 1. As the table shows, all the intrinsic viscosities somewhat increased with the rate of shear over the range of 200–1200 sec^{-1} within the limit of experimental error. Although each plot of $\log(\eta_{sp}/c)$ versus c was linear, as Fig. 2

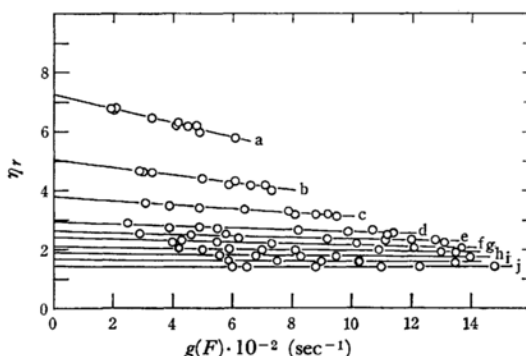


Fig. 1. Shear rate dependence of the relative viscosity of methylcellulose solution at 45°C; a, 0.3030 g/100 ml; b, 0.2424; c, 0.2020; d, 0.1731; e, 0.1515; f, 0.1359; g, 0.1212; h, 0.1010; i, 0.0866; j, 0.0606.

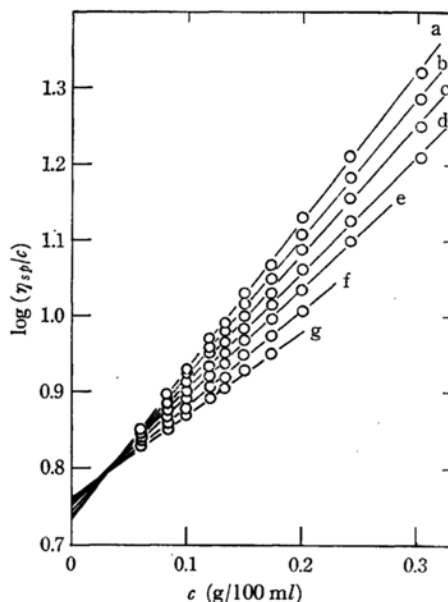


Fig. 2. Martin's plots of methylcellulose solution at 45°C; a, $g(F)=0 \text{ sec}^{-1}$; b, 200; c, 400; d, 600; e, 800; f, 1000; g, 1200.

shows, $\log(\eta_{sp}/c)$ decreased with the rate of shear in this experimental range. Accordingly, the positive

23) G. W. Scott Blair, "Foodstuffs, Their Plasticity Fluidity and Consistency," North-Holland Pub. Co., Amsterdam (1953).

24) H. M. Spurlin, A. F. Martin and H. G. Tennet, *J. Polymer Sci.*, **1**, 63 (1946).

TABLE 2. HUGGINS' CONSTANT OF DILUTE AQUEOUS SOLUTION OF METHYLCELLULOSE

T ($^{\circ}\text{C}$)	$g(F)$ (sec^{-1})						
	0	200	400	600	800	1000	1200
25	0.398	0.332	0.249	0.256	—	—	—
30	0.525	0.395	0.371	0.330	0.240	—	—
35	0.577	0.443	0.393	0.337	0.240	—	—
40	0.638	0.501	0.458	0.423	0.417	0.327	—
45	0.820	0.765	0.698	0.629	0.590	0.514	0.447

rate-shear dependence of $[\eta]_{g(F)}$ can be concluded to have been obtained on the assumption that Martin's plots are linear down to an infinite dilution. The positive rate-shear dependence of $[\eta]_{g(F)}$ obtained on this assumption was similar to those of aroclor solutions of polymethylmethacrylate,²¹ although the highest value of the $[\eta]_{g(F)}/[\eta]_{g(F)=0}$ ratio in our case was 1.08 at 30°C , $g(F)=800\text{ sec}^{-1}$, while that in a polymethylmethacrylate solution was over 2.0. Peterlin⁹ has predicted that, in an extreme case in which the usual flexible polymer molecule is very long and the solvent is extremely viscous, the intrinsic viscosity would be expected to increase with the shear gradient over a limited range. In our case, however, the first condition of the polymer molecule being very long was not met; the molecular weight of this methylcellulose was calculated to be about $(3-4) \times 10^5$ by using the relationship between the intrinsic viscosity and the molecular weight reported in Ref. 4. The molecule with a molecular weight of about $(3-4) \times 10^5$ cannot be considered to be very long. On the other hand, the viscosity of the solvent, water, is about 1 centi-poise at 20°C and so is not very large, either. Therefore, the shear-rate dependence of the intrinsic viscosity of a methylcellulose solution seems to be due to the small flexibility of the chain. In general, cellulose derivatives have a relatively extended form in solution and take the configuration of the free draining model. The increase in the intrinsic viscosity with the rate of shear is considered to come from the specific property of the cellulose derivative.

The constant, k , in Martin's equation is related to Huggins' constant, k' , as $k=k'/2.3$. The values of k' obtained at constant $g(F)$ are shown in Table 2. These values decreased with $g(F)$ and increased with the temperature. Uda⁴ has reported that the Huggins' constant of a dilute solution of methylcellulose decreased with the temperature over the range from 20°C to 45°C . However, his values were not those at a constant rate of shear. Since the flow time in the capillary decreases exponentially with an increase in the temperature and as, consequently, the rate of shear increases, the correction of the rate of shear may be necessary for any discussion of the temperature dependence of k' . Furthermore, the fact that the increase in k' comes from a decrease in solubility seems to support the positive temperature dependence of k' .

Generally the intrinsic viscosity of cellulose derivatives has a large negative temperature coefficient. Some workers²⁵⁻²⁸ have attributed this behavior to the increase in the flexibility of chain, and others⁴ to the decrease in the degree of hydration, with the increase in temperature. In view of the fact that the solubility decreased with the temperature, as has been described above, the latter interpretation seemed to be more reasonable. For the value of $-d[\eta]/dT$ where T is the temperature, values of 0.28–0.31 (100 ml/g·deg) were obtained over the range of the rate of shear from 200 to 800 sec^{-1} ; these values are shown in Table 1. Since the value of $d[\eta]/dT$ decreased with the $g(F)$, the methylcellulose molecule in a dilute solution seems to be not sphere but an ellipsoid and it seems to correspond with the increase in intrinsic viscosity described above.

Kahn and Witnauer²⁹ pointed out that the energy of the activation of flow and the entropy of flow would be measures of the particle alignment in a solution; they treated their viscosity data according to the theory of rate process.³⁰

According to Eyring's theory,³⁰ the viscosity is given by the following equation:

$$\eta = (Nh/V) \exp(-\Delta S/R) \exp(E_v/RT), \quad (4)$$

where N is Avogadro's number, h is Planck's constant, V is the molar volume of the solute, ΔS is the entropy of flow, R is the gas constant, E_v is the energy of the activation of flow, and T is the absolute temperature. From Eq. (4) we have:

$$\ln \eta = \ln(Nh/V) - (\Delta S/R) + E_v/RT. \quad (5)$$

Some examples of the plots of $\log \eta$ versus $(1/T)$ are shown in Fig. 3. The values of E_v were calculated from the slopes of the plots. The values of E_v obtained are shown in Table 3. From Table 3 it is

25) L. Mandelkern and P. J. Flory, *J. Am. Chem. Soc.*, **74**, 2517 (1952).

26) H. Maeda, T. Kawai and K. Saito, *Chem. High Polymer (Japan)*, **15**, 610 (1958).

27) P. J. Flory, O. K. Spurr and D. K. Carpenter, *J. Polymer Sci.*, **27**, 231 (1958).

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

29) L. D. Kahn and L. P. Witnauer, *J. Biol. Chem.*, **241**, 1784 (1966).

30) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York (1941).

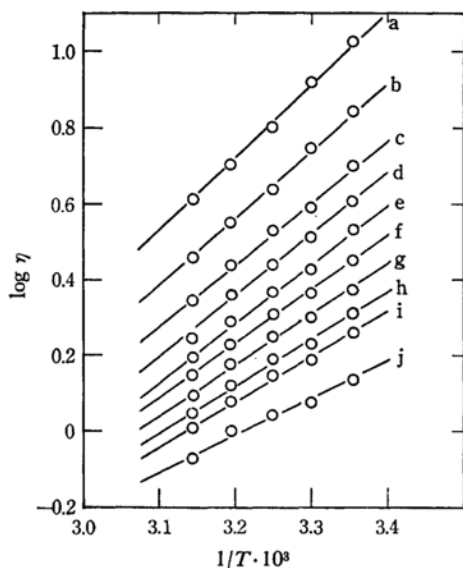


Fig. 3. Plots of $\log \eta$ of methylcellulose solution versus $1/T$ at $g(F)=200 \text{ sec}^{-1}$; a, 0.3030 g/100 ml; b, 0.2424; c, 0.2020; d, 0.1731; e, 0.1515; f, 0.1359; g, 0.1212; h, 0.1010; i, 0.0866; j, 0.0606.

clear that a high energy is required for the flow in the high-concentration range and at a low rate of shear. The values of E_v obtained in this system were somewhat higher than the 5.8 kcal obtained in the aqueous solution of solubilized calf-skin collagen.²⁰ From these results, it seems that methylcellulose shows a strong tendency toward alignment

TABLE 3. THE ENERGY OF ACTIVATION OF FLOW OF METHYLCELLULOSE SOLUTION, E_v , (kcal)

c (g/100 ml)	$g(F)$, (sec^{-1})				
	0	200	400	600	800
0.0606	5.00	4.67	4.72	4.72	4.58
0.0866	6.10	5.68	5.55	5.09	5.04
0.1010	7.33	5.82	5.73	5.68	5.68
0.1212	7.88	6.32	6.19	5.91	5.96
0.1359	8.02	6.65	6.78	6.74	6.42
0.1515	8.11	7.24	7.20	7.10	—
0.1731	8.34	7.33	7.38	—	—
0.2020	8.80	7.65	7.61	—	—
0.2424	9.03	8.25	—	—	—
0.3030	9.72	8.80	—	—	—

with a flowing stream. The statement seems to be essentially consistent with the shear-rate dependence of $[\eta]$ and $d[\eta]/dT$ described above. For lack of the value of the molar volume of methylcellulose, however, the entropy of flow could not be discussed here. The effects of the molecular weight and the molecular-weight distribution on the non-Newtonian viscosity of the dilute solution are also awaiting discussion. The non-Newtonian viscosity of the dilute aqueous solution of methylcellulose, however, seems to come from the small flexibility of the chain and from a strong tendency toward alignment with a flowing stream.

The authors are grateful to Shinetsu Chemical Ind. for supplying the sample of methylcellulose (trade name "Metolose 90 SH 15000").