

## Some Solution Properties of Fractionated Water-Soluble Hydroxypropylcellulose\*

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### Synopsis

A solution-fractionation technique has been developed for water-soluble (molar substitution, MS, ca. 4) hydroxypropylcellulose (HPC), utilizing mixtures of anhydrous ethanol (solvent) and *n*-heptane (nonsolvent) of varying composition. Solubility is primarily an inverse function of chain length, species of highest molecular weight being soluble only in solvent mixtures richest in ethanol. Fractionation data indicate HPC substitution is fairly uniform, although there is a tendency for shorter chains to be more highly substituted than long ones. Some control over the degree of variation is possible by changes in processing conditions. Molecular weight and molecular weight distribution reflect the properties of the cellulose employed in sample preparation and the use or omission of deliberate degradation for viscosity control. A sample of HPC ( $[\eta] = 4.2$ ; MS = 4.4) was separated into seven fractions of approximately equal weight and the average molecular weight ( $M_w$ ), root mean square radius of gyration, and second virial coefficient of each of these fractions in ethanol were determined by light scattering, while molecular weight distributions were investigated by gel permeation chromatography in tetrahydrofuran. The relation between intrinsic viscosity and degree of polymerization ( $DP$ ) was found to be  $[\eta] = 7.2 \times 10^{-3} \overline{DP}_w^{0.90}$ . A comparison of hydrodynamic and configurational parameters for HPC in ethanol with those for hydroxyethylcellulose (HEC) in water indicates these two polymers behave very similarly in solution. In both systems the ratio of the mean square end-to-end unperturbed molecular chain length ( $R_0^2$ ) to  $DP$  diminishes with increasing molecular weight, reaching a minimum at a  $DP_w$  of approximately 3000. The ratio  $[(\overline{R_0^2})/(\overline{R_g^2})]_z^{1/2}$ , where  $(\overline{R_g^2})^{1/2}$  is the root mean square end-to-end distance for 1,4'-polysaccharides assuming free rotation of the chain units, also diminishes with increasing molecular weight, reaching a limiting value of 3.5. This relatively high ratio indicates considerable rigidity in the coiled molecule and is believed to be at least partially the result of intramolecular hydrogen bonding.

### INTRODUCTION

Nearly all polymers, both natural and synthetic, are polydisperse in nature, and cellulose is no exception. Depending on its source and mode of handling, purified cellulose may contain molecules varying in molecular weight from a few thousand to a few million. Usually the molecular size of cellulose and its derivatives is expressed in terms of the degree of poly-

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merization ( $DP$ ), the average number of anhydroglucose monomer units in the polymer chains.

Cellulose derivatives, normally esters or ethers, are formed by appropriate reaction with the three available hydroxyl groups on each monomer unit, the extent of reaction being described as the degree of substitution ( $DS$ ), the average number of these three hydroxyls substituted. An added complication arises when the substituent groups contain a hydroxyl, as in the case of such ethers as hydroxyethylcellulose (HEC) and hydroxypropylcellulose (HPC), permitting the formation of poly(1,2-alkyleneoxy) side chains. (Hydroxypropylcelluloses are marketed by Hercules Incorporated under the registered trade name Klucel.) In these materials, three hydroxyl groups are always available per anhydroglucose unit, regardless of the amount of substituent added. For this reason, the substitution of such polymers is expressed in terms of the molar substitution ( $MS$ ), the average number of moles of reactant combined per mole of monomer units. Whereas the maximum possible  $DS$  of a cellulose derivative is 3, there is no theoretical limit to the  $MS$ . The properties of this type of polymer are not only influenced by polydispersity, but by the extent and uniformity of substitution as well.

This paper describes the fractionation of four HPC samples of  $MS$  ca. 4 and a study of some of the dilute solution properties of the components of one of them. Polymer fractionation theory and technique have been the subject of several recent excellent surveys and discussions.<sup>1-4</sup> Accounts of cellulose ether fractionation appearing in the literature include those of Signer and Liechti,<sup>5</sup> Timell and Purves,<sup>6</sup> Uda and Meyerhoff,<sup>7</sup> Smith,<sup>8</sup> and Simionescu et al.<sup>9</sup> for methylcellulose; Timell,<sup>10</sup> Sitaramaiah and Goring,<sup>11</sup> Brown et al.,<sup>12</sup> and Rinaudo<sup>13</sup> for sodium carboxymethylcellulose; Brown<sup>14</sup> for HEC; and Manley<sup>15</sup> for ethylhydroxyethylcellulose. Of the two most commonly used preparative fractionation methods, fractional solution was selected for the studies described herein because it possesses two inherent advantages over its counterpart, fractional precipitation: (1) smaller ratios of liquid volume to polymer weight are required, and (2) higher molecular weight fractions are less contaminated with low molecular weight polymer.<sup>16,17</sup>

In addition to establishing a relationship between intrinsic viscosity  $[\eta]$  and molecular weight (or  $DP$ ) for HPC, solution property measurements included in this study are concerned with the configuration of molecules of this polymer in anhydrous ethanol, one of its better solvents.

## EXPERIMENTAL

### Fractionation

The fractional solution technique developed for the fractionation of HPC utilizes stepwise extraction directly from flake polymer by mixtures of anhydrous ethanol (solvent) and *n*-heptane (nonsolvent) at 30°C for periods

of 16 hr or more with continuous agitation. At the completion of each extraction, the undissolved material in the form of discrete translucent gel particles is separated from the supernatant liquid by decantation and/or centrifugation. The clear solution is concentrated on a steam bath under a nitrogen blanket until it becomes sufficiently viscous to spread, as a paste, on the surface of a piece of Teflon sheeting. The film is then vacuum dried (3 hr at 60°C), stripped from the Teflon, and weighed.

An alternative method for recovering fractions from extract solutions is based on addition of sufficient water to cause separation into two layers. Most of the fraction is concentrated in the heavier ethanol-water layer from which it may be obtained by freeze-drying. Several water washes of the ethanol-heptane layer permit almost total recovery of the remainder of the fraction.

In either case, the undissolved material is extracted subsequently with the next richer solvent-nonsolvent blend by first dispersing it in a mixture corresponding to the composition of the previous blend and then adding additional ethanol, with vigorous agitation, to give the desired final composition. This procedure eliminates agglomeration of swollen polymer particles.

The most useful range of alcohol concentration for the fractional solution of HCP is 30 to 50% by weight (see Fig. 1). Samples of high MS are relatively more soluble at low ethanol concentrations than those of low MS.

In a typical fractionation, an initial charge of approximately 8 g (dry basis) of polymer (particle size <30 mesh) is used, together with 400-g portions of extractant. Equilibrium or pseudoequilibrium conditions have been demonstrated by essentially constant solids content of each extractant mixture after 16 hr. It is possible that absolute thermodynamic equilibrium is not attained in this period at the highest molecular weights, but the degree of fractionation achieved by this procedure is quite satisfactory for most purposes. Manley,<sup>15</sup> in a fractional solution study of ethylhydroxyethyl-

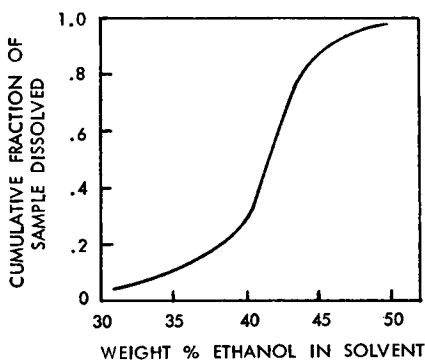


Fig. 1. Typical solubility curve for MS = 4 hydroxypropylcellulose in ethanol-*n*-heptane mixtures.

cellulose, reported that an extraction period as long as two weeks at 20°C was necessary to establish equilibrium in the case of fractions of high DP; however, his solvent/polymer ratio was only half that used in this investigation.

### Intrinsic Viscosity

Intrinsic viscosities,  $[\eta]$ , were determined from plots of  $\log(\eta_{sp}/c)$  versus  $c$  by means of Martin's equation

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

which fitted experimental data far better than Huggins' equation

$$\eta_{sp}/c = [\eta] + k' [\eta]^2 c.$$

Measurements were made in Ubbelohde viscometers at 25°C in water, ethanol, or 50:50 water:ethanol (v/v); no shear rate corrections were made. Essentially identical values of  $[\eta]$  were obtained in these three solvent systems. Analysis of viscosity data indicated a consistent Martin constant of 0.18 which permitted the development of a one-point intrinsic viscosity method.<sup>18</sup> Unless otherwise stated, intrinsic viscosity data reported herein were determined in water-ethanol.

### Substitution

HPC substitution (MS) was determined by a slight modification of the terminal methyl group method of Lemieux and Purves.<sup>19</sup>

### Light Scattering

Light scattering techniques were used to determine weight-average molecular weights,  $M_w$ ,  $Z$ -average radii of gyration,  $(\overline{S^2})_z^{1/2}$ , and second virial coefficients,  $A_2$ , as described in the literature.<sup>20</sup>

A SOFICA photogoniometer was used for the light-scattering measurements. This instrument, designed by Wippler and Scheibling,<sup>21</sup> is characterized by an exceedingly fine optical system and a very steady, high-intensity mercury arc light source. Residual fluctuations in light intensity are compensated for by a reference photomultiplier which samples a portion of the incident light beam. Excellent temperature control is achieved by use of a liquid bath. Since the cell and optics are also immersed in this bath, which is filled with a liquid having a refractive index close to that of glass (toluene,  $n = 1.49$ , is normally used), corrections due to reflections at air-glass interfaces are eliminated. Depolarization corrections were found to be negligible for the system studied, and fluorescence was absent.

The necessary calculations were made with the aid of an SDS 920 computer, and the resulting data were plotted by a Calcomp 565 graph plotter operated by the computer. These expedients resulted in a great saving of time and meant that the number of samples that could be examined in any given period was limited only by the time necessary to clarify solutions. However, the extrapolation of plotted data was done manually.

The instrument was calibrated with several polystyrene fractions, of both broad and narrow molecular weight distributions, obtained from the National Bureau of Standards. The operation of the instrument was checked by means of carefully filtered dilute Ludox colloidal silica suspensions and fluorescein solutions. Measurements were carried out at a wavelength of 546 m $\mu$  and at a temperature of 25°C.

All solutions and solvents used for light scattering were clarified by means of ultrafiltration through membrane filters (obtained from Millipore Filter Corporation, Bedford, Mass.) with a mean pore size of 0.45  $\mu$ . With these filters, dissymmetry ratios,  $Z = (I_{45}/I_{135})$ , of organic solvents such as toluene and benzene were near 1.00 and always less than 1.03. However, for solvents such as water and alcohol these low values of  $Z$  could not be realized, but the ratio was still in the region 1.10 to 1.15. Fortunately, the excess scattering of the solutions in these solvents was so high, at least four times the solvent scattering, that solvent dissymmetry had little adverse effect.

Unfortunately, samples of the highest molecular weight could not be filtered even when filters of much larger pore size were used. The molecular weights of these samples were obtained from gel permeation chromatography (GPC) data, as described below. As a result,  $(\bar{S}^2)_z^{1/2}$  and  $A_2$  could not be determined for these samples.

### Refractive Index Increment

Values of the specific refractive increment,  $dn/dc$ , for the samples used were obtained by means of a Waters R-4 differential refractometer. The sensitivity of this instrument approaches that of a high-quality interferometer. A refractive index change of  $1 \times 10^{-7}$  or  $2 \times 10^{-7}$  can be measured readily. The instrument was calibrated with solutions of NaCl, KCl, sucrose, Na<sub>2</sub>SO<sub>4</sub>, and maltose hydrate at the same concentrations as those of the HPC solutions studied. For calibration purposes, the values of the refractive index listed by Kruis<sup>22</sup> were used for KCl, NaCl, and Na<sub>2</sub>SO<sub>4</sub>. Values for sucrose and maltose hydrate were taken from the *Handbook of Chemistry and Physics*,<sup>23</sup> although, unfortunately, only data for concentrations higher than those used are listed in this reference. In the case of these materials, the  $dn/dc$  determined at these higher concentrations was assumed to be valid for the concentration range of interest as well.

For HPC in anhydrous ethanol at 25°C,  $dn/dc$  at 546 m $\mu$  was found to be 0.120 for the concentration range 0.1 to 0.5 g/dl.

### Gel Permeation Chromatography

The instrument used for GPC studies was a Waters gel permeation chromatograph which has been described adequately in the literature.<sup>24</sup> Four columns of crosslinked polystyrene gels swollen in tetrahydrofuran (THF) were employed. The gels were designated by nominal pore diameters of  $2 \times 10^3$ ,  $3 \times 10^4$ ,  $10^5$ , and  $1.5 \times 10^6$  Å. Solution concentrations were

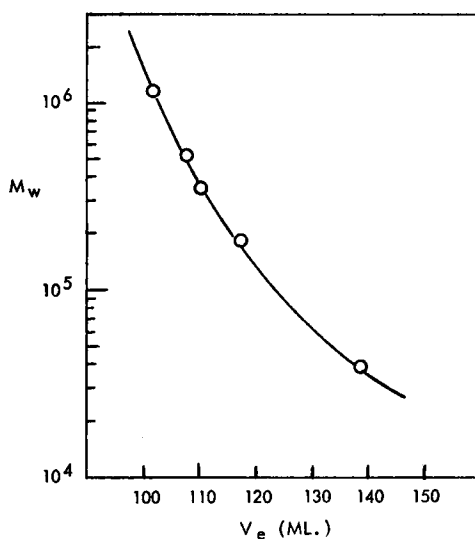


Fig. 2. GPC calibration curve for hydroxypropylcellulose in tetrahydrofuran.

0.5% in THF, and 2-ml aliquots were introduced into the first column and flushed through with THF. The flow rate was 1 ml/min and the operating temperature of the columns was 25°C.

Unfortunately, there are no HPC samples of narrow molecular weight distribution to serve as calibration standards. Accordingly the instrument was calibrated first with NBS polystyrene standards, as described in the Waters manual. This calibration curve was used to determine the  $M_w/M_n$  ratios of all the HPC fractions. Then the available light-scattering  $M_w$  values were plotted against the corresponding peak elution volumes,  $V_e$ , to obtain a new calibration curve (shown in Fig. 2) which was used to determine the  $M_w$  of samples that could not be filtered for light scattering. For calculation of the  $M_w/M_n$  ratios, an SDS computer again was employed.

## RESULTS AND DISCUSSION

### Fractionation Data

The four HPC samples fractionated in this study included two (samples A and B) prepared under identical conditions from different celluloses; a third (sample C), representing essentially a duplicate of one (sample B) of these, which had been deliberately peroxide degraded to reduce its solution viscosity; and a fourth (sample D), similar to the third, but prepared from a slightly different cellulose by a modified procedure designed to give a broader range of substitution. The last sample was studied in more detail than the first three. Fractionation results are summarized in Tables I to IV, inclusive. The tabular data include the ethanol content of the extractants, the corresponding weight fractions dissolved, and the average

TABLE I  
Fractionation Data for Sample A

Frac- tion	Ethanol in solvent, wt-%	Fraction wt, g	Weight fraction		[ $\eta$ ], dl/g	Est. $\overline{DP}_w$	MS
			Incre- mental	Cumu- lative			
1	37	0.303	0.038	0.038	0.53	120	4.20
2	41.5	1.433	0.178	0.216	2.63	700	4.25
3	42.75	2.412	0.299	0.515	4.64	1300	4.35
4	43.75	1.307	0.162	0.677	5.55	1600	4.35
5	44.5	0.950	0.188	0.795	6.52	1900	4.25
6	46.5	1.251	0.155	0.950	7.07	2100	4.20
7	100	0.404	0.050	1.000	7.35	2200	3.75
Weighted Av.					5.0		4.25
Whole Polymer					5.0	1400	4.15

TABLE II  
Fractionation Data for Sample B

Frac- tion	Ethanol in solvent, wt-%	Fraction wt, g	Weight fraction		[ $\eta$ ], dl/g	Est. $\overline{DP}_w$	MS
			Incre- mental	Cumu- lative			
1	29	0.414	0.051	0.051	0.14	27	4.65
2	38	1.155	0.143	0.194	0.65	150	4.30
3	41	1.317	0.163	0.357	1.93	500	4.10
4	43	1.894	0.235	0.592	4.42	1200	4.20
5	45.5	1.208	0.150	0.742	6.65	2000	4.10
6	49	0.954	0.118	0.860	8.43	2500	3.95
7	100	1.123	0.140	1.000	11.72	3600	3.85
Weighted Av.					5.1		4.15
Whole Polymer					5.0	1400	4.30

TABLE III  
Fractionation Data for Sample C

Frac- tion	Ethanol in solvent, wt-%	Fraction wt, g	Weight fraction		[ $\eta$ ], dl/g	Est. $\overline{DP}_w$	MS
			Incre- mental	Cumu- lative			
1	34	0.708	0.088	0.088	0.20	40	4.65
2	39.5	1.380	0.171	0.259	1.11	270	4.20
3	41	1.146	0.142	0.401	2.48	650	3.95
4	42.25	1.736	0.215	0.616	4.46	1250	3.80
5	44.75	2.061	0.256	0.872	7.45	2200	3.65
6	49.5	0.815	0.101	0.973	8.12	2400	3.55
7	100	0.213	0.027	1.000	9.26	2800	3.50
Weighted Av.					4.5		3.90
Whole Polymer					4.4	1230	3.85

TABLE IV  
 Fractionation Data for Sample D

Frac- tion	Ethanol in solvent, wt-%	Fraction wt, g	Weight fraction		$[\eta]$ , dl/g	Est. $\overline{DP}_w$	MS
			Incre- mental	Cumu- lative			
1	35.8	1.171	0.145	0.145	0.22	44	5.20
2	39.5	1.368	0.170	0.315	1.46	370	4.70
3	40.2	1.500	0.186	0.501	2.18	560	4.45
4	40.8	0.862	0.107	0.608	3.31	900	4.30
5	41.6	0.962	0.119	0.727	5.20	1500	4.20
6	42.3	1.243	0.154	0.881	8.30	2500	4.10
7	100	0.957	0.119	1.000	9.75	3000	4.00
Weighted Av. Whole Polymer					4.1		4.45
					4.2	1170	4.40

substitution, intrinsic viscosity, and estimated degree of polymerization (based on a relationship developed in a subsequent section of this paper) of each of the fractions.

In general, all fractionations appear to be satisfactory in that high sample recoveries (>99% of an initial charge of 8.1 g) were obtained, and weighted averages of  $[\eta]$  and MS of the fractions check, within reasonable limits, the corresponding values for the whole polymers. Apparently fractionation by this technique is based on solubility differences due primarily to variations in molecular chain length. The substitution of HPC appears to be fairly uniform, although there is a tendency for the MS of shorter molecular chains to be higher than that of longer ones. A comparison of the integral distribution curves for samples A, B, and C is given in Figure 3.

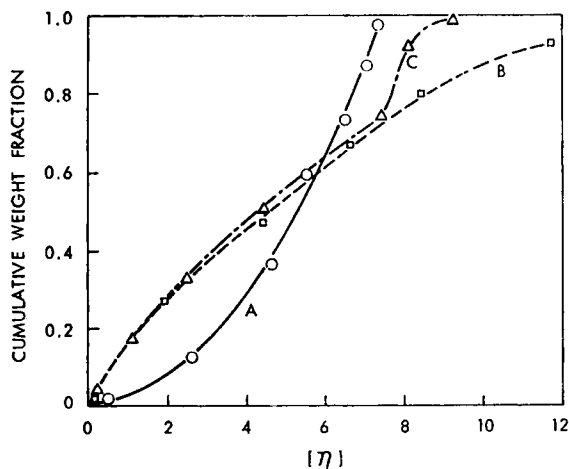


Fig. 3. Comparison of integral weight distribution curves from fractionation of samples A, B, and C.



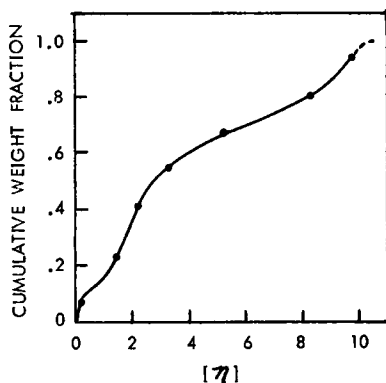


Fig. 4. Integral weight distribution curve from fractionation of sample D.

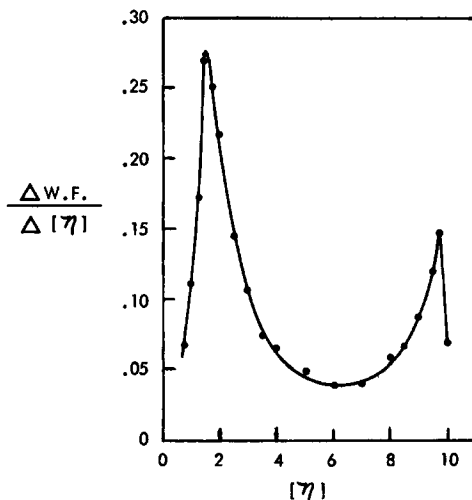


Fig. 5. Differential weight distribution curve for sample D (obtained by graphical differentiation of Figure 4).

Although whole polymers A and B have the same intrinsic viscosity (5.0 dl/g), it is obvious from these plots that the latter contains a much broader range of molecular sizes than the former. This variation is attributed to the inherent characteristics of the different celluloses used in their preparation.

The shape of the integral distribution curve for sample C reflects the results of viscosity reduction. Comparison with the curve for the corresponding undegraded sample B reveals that the effect of random degradation is most pronounced at the high molecular weight end, as would be expected.

The integral distribution curve for sample D (Fig. 4) indicates that this particular polymer contains an appreciable amount of low molecular weight material. The differential distribution curve for this sample

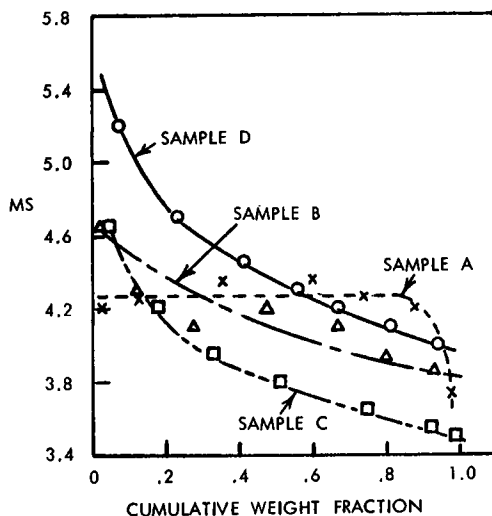


Fig. 6. Variation in substitution of fractions derived from four hydroxypropylcellulose samples.

(Fig. 5) suggests a bimodal distribution similar to that reported by Manley<sup>15</sup> for ethylhydroxyethylcellulose. The portion of this curve below an intrinsic viscosity of 0.75 is not shown, as additional fractionation data would be required to define its contour precisely.

### Substitution of Fractions

The variation in average substitution among fractions, depicted graphically in Figure 6, has already been mentioned. If samples B and C are considered standard HPC preparations, then a substitution differential of 0.7 to 1.0 MS unit between extremes appears normal. However, by altering processing conditions, a greater spread in substitution may be obtained, if desired, as illustrated by sample D. Other lots, similar to D, have exhibited MS differentials as great as 1.7 units.

On the other hand, by proper selection of a suitable cellulose, as in the case of sample A, it is possible to prepare an essentially uniformly substituted HPC. Only the MS of the very last (highest molecular weight) fraction of this preparation differs significantly from that of the mean for the whole polymer.

### Light Scattering and GPC Data

Light scattering and GPC measurements were made not only on sample D and each of its seven fractions, but on six selected fractions from other samples as well, in order to secure information over as broad a molecular weight range as possible with minimal variations in substitution. (Because of solution clarification difficulties, previously mentioned, light scattering measurements could not be made on two of the 13 fractions.) Data obtained are listed in Table V.

TABLE V  
Summary of GPC and Light Scattering Data for HPC Fractions

Fraction	$[\eta]$ , dl/g	$\overline{DP}_w$	$M_w \times 10^{-3}$	$M_w/M_n$	$(\overline{S^2})_z^{1/2}$ , Å	$A_z \times 10^4$ , ml mole g <sup>-1</sup>
D1	0.22	84	39	1.90	210	23.2
D2	1.46	420	183	1.58	435	11.6
D3	2.18	610	256	1.78	405	9.0
D4	3.31	850	350	1.94	450	8.2
D5	5.20	1280	520	2.10	680	7.7
D6	8.30	2900	1160	2.42	935	5.9
D7	9.75	3200	1260	2.51	—	—
D (whole polymer)	4.20	1000	416	11.6	—	—
I	0.64	179	74	1.27	245	18.2
II	1.21	267	106	1.46	230	13.8
III	4.30	1000	410	2.02	580	8.0
IV	7.14	2280	950	2.37	855	7.7
V	8.40	2690	1050	2.40	—	—
VI	11.80	3380	1430	2.55	1050	5.6

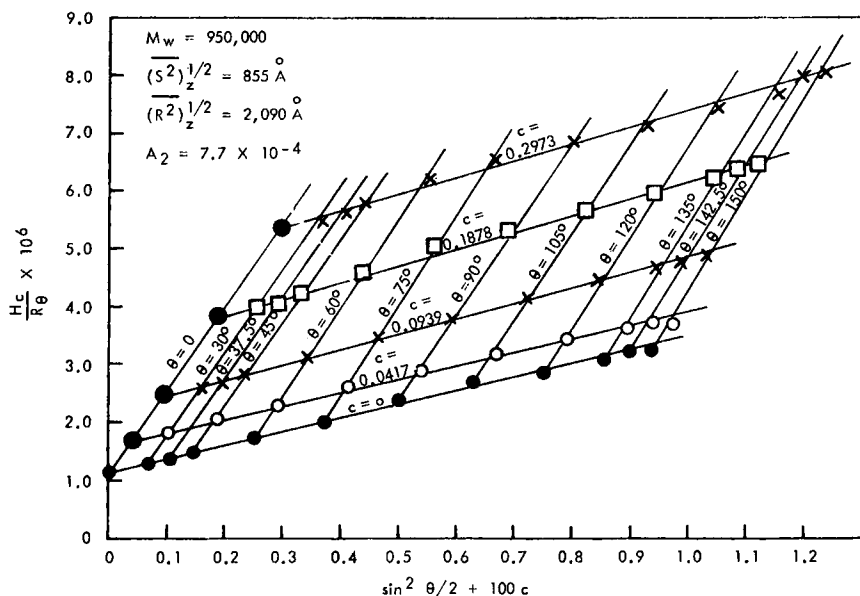


Fig. 7. Zimm plot of light scattering data on fraction IV in ethanol.

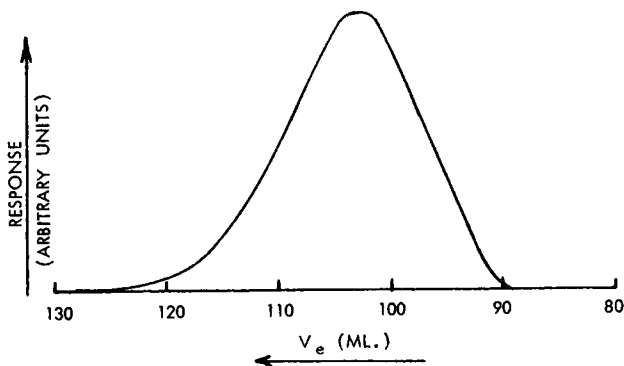


Fig. 8. GPC curve for hydroxypropylcellulose fraction D6.

A typical Zimm plot is shown in Figure 7. The absence of unusual features, such as excessive curvature, indicates that the solution was dust free and the molecular weight distribution (MWD) was not too broad. The procedures for calculating  $M_w$ ,  $(\overline{S^2})_z^{1/2}$ , and  $A_2$  are adequately described in the literature<sup>20</sup> and need not be detailed here.

Figure 8 shows a typical GPC trace (sample D6); this particular fraction has a  $M_w/M_n$  ratio of approximately 2.4. The polydispersity of the fractions appears to increase slightly with molecular weight, the  $M_w/M_n$  values ranging from 1.5 to 2.5 for the components of sample D. The GPC trace for the whole polymer, which confirms the bimodal distribution indicated by fractionation data, can be very closely approximated by normalizing and

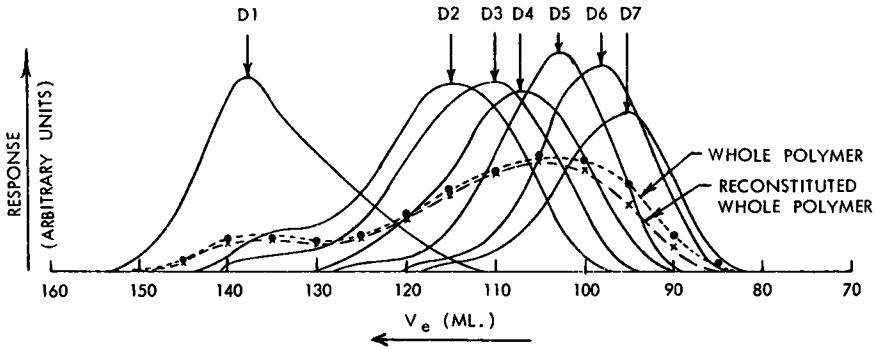


Fig. 9. Comparison of GPC curve for hydroxypropylcellulose sample D with that obtained by summing curves for fractions.

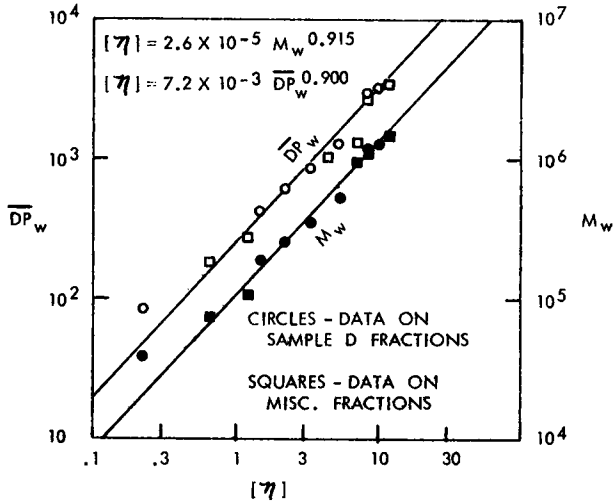


Fig. 10. Relation between intrinsic viscosity and molecular size for hydroxypropylcellulose.

summing the curves for its seven fractions, as demonstrated in Figure 9.

Figure 10 illustrates the relation between  $[\eta]$  (in ethanol) and molecular size for HPC, both in terms of weight-average molecular weight and weight-average degree of polymerization. The best straight lines representing the experimental points are described by the following equations:

$$[\eta] = 2.6 \times 10^{-5} M_w^{0.915}$$

$$[\eta] = 7.2 \times 10^{-3} \overline{DP}_w^{0.900}$$

In both cases, data for fraction D1 were ignored, as its composition is definitely atypical. The appreciably higher-than-average substitution of this fraction apparently causes a deviation from normal solution behavior.

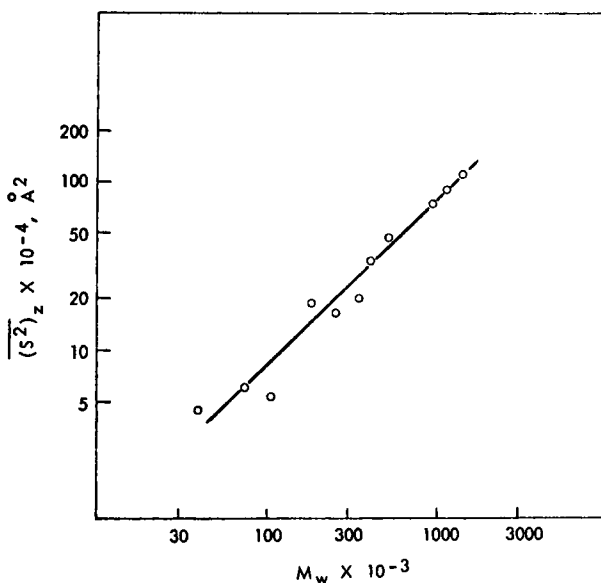


Fig. 11. Relation between mean square radius of gyration and molecular weight of hydroxypropylcellulose fractions.

The relatively high values of the exponential terms in the above equations indicate that HPC molecules in ethanol must be rather highly extended. The slight difference in magnitude of these terms is the result of a variation in MS with  $M_w$  among the fractions considered.

The mean square radius of gyration,  $(\overline{S^2})_z$ , is plotted against the weight-average molecular weight of each of the 11 HPC fractions for which such information is available in Figure 11. The equation of the straight line corresponds to

$$(\overline{S^2})_z = 0.85 M_w^{0.977}.$$

The slope of this line is nearly the same as that (0.96) which Brown<sup>25</sup> reported for HEC fractions in water. The scatter of experimental points may be due, at least in part, to variations in MS and polydispersity among the fractions.

The Gaussian coil model, generally accepted for molecules of linear flexible chain molecules in solution, dictates the following relation between the root mean square end-to-end distance,  $(\overline{R^2})_z^{1/2}$ , and the radius of gyration:

$$(\overline{R^2})_z^{1/2} = 6^{1/2} (\overline{S^2})_z^{1/2}.$$

Additionally, Flory and Fox<sup>26,27</sup> have described the dependence of intrinsic viscosity on other molecular parameters as

$$[\eta] = \Phi (\overline{R_0^2}/M)^{1/2} M^{1/2} \alpha^3$$

where  $(\overline{R_0^2})^{1/2}$  is the root mean square end-to-end distance,  $\alpha$  is the molecular expansion factor, and  $\Phi$  is a constant for randomly coiling molecules

independent of solvent and polymer. However, for many cellulose derivatives,  $\Phi$  varies with chain length and approaches the usually accepted value (approximately  $2.2 \times 10^{21}$ ) as an asymptotic limit at high molecular weights. In terms of measurable experimental quantities, the above equation may be rewritten as

$$\Phi = q[\eta]M_w/(\overline{R^2})_z^{1/2}$$

where  $(\overline{R_0^2})^{1/2}\alpha$  has been replaced by  $(\overline{R^2})_z^{1/2}$ , and the factor  $q$  has been introduced to compensate for polydispersity. The correction factor  $q$  has been discussed at considerable length elsewhere.<sup>28-31</sup> It was calculated by use of the following equation:

$$q = \frac{(h+2)^{1/2}}{(h+1)^2} \cdot \frac{\Gamma(h+2)}{\Gamma(h+1.5)}$$

which is based on the assumption that the polydispersity of the fractions may be described by the following ratios:

$$M_z:M_w:N_n = (h+2):(h+1):h.$$

These ratios also provided a means to calculate an estimated  $M_z$  from  $M_w$  and  $M_n$ .

A comparison of the hydrodynamic behavior of HPC in ethanol with that of HEC in water<sup>25</sup> is given in Table VI in terms of the variation of  $\Phi$  with  $M_w$ . It is obvious that these two systems are very similar and that the asymptotic value of  $\Phi$  is approached only at a  $\overline{DP}_w$  of ca. 3000 or above.

The molecular expansion factor  $\alpha$  was calculated by means of the following equation attributed to Orofino and Flory<sup>32</sup>:

$$A_2 = \left(\frac{16\pi}{3^{1/2}}\right) \cdot \left(\frac{N(\overline{S^2})_z^{1/2}}{M_z^2}\right) \cdot \ln \left[1 + \frac{\pi^{1/2}}{2}(\alpha^2 - 1)\right].$$

The  $\alpha$  values listed in Table VII were derived from the second virial coefficients  $A_2$  tabulated in Table V. The latter decrease with increasing molecular weight, as observed by Brown et al.<sup>25</sup> for HEC in water. Molecular expansion factors for HPC in ethanol (1.13 to 1.26) are intermediate between those for HEC in water (1.04 to 1.08) and cadoxen (1.09 to 1.42).<sup>25</sup>

The unperturbed root mean square end-to-end distance  $(\overline{R_0^2})_z^{1/2}$  for each HPC fraction in ethanol was calculated from the relation

$$(\overline{R_0^2})_z^{1/2} = (\overline{R^2})_z^{1/2}/\alpha$$

and from these data the corresponding configurational parameters  $(\overline{R_0^2}/DP)_z$  were determined. These quantities are tabulated in Table VII and compared with the corresponding, previously reported<sup>25</sup> values for HEC in water. Again, it appears that the two polymers in their respective solvents behave almost identically. The parameter  $(\overline{R_0^2}/DP)_z$  increases with decreasing chain length, indicating a transition from a

TABLE VI  
Variation of  $\phi$  with Increasing Molecular Chain Length for HPC in Ethanol and HEC in Water

Fraction	$\overline{DP}_w$	$(\overline{S^2})_z \times 10^{-4}, \text{\AA}^2$	$(\overline{R^2})^{1/2}, \text{\AA}$	$h$	$\frac{(h+2)}{(h+1)} = \frac{M_z}{M_w}$	$q$	$\phi \times 10^{-21}$
HPC in Ethanol							
D2	420	14.3 <sup>a</sup>	925	1.725	1.37	1.68	0.6
D3	610	20.0 <sup>a</sup>	1090	1.285	1.44	1.82	0.8
D4	850	27.2 <sup>a</sup>	1280	1.065	1.485	1.915	1.1
D5	1280	40.0 <sup>a</sup>	1550	0.910	1.525	2.005	1.5
D6	2900	87.5 <sup>a</sup>	2290	0.705	1.585	2.15	1.7
HEC in Water <sup>b</sup>							
C11	340	—	745	1.925	1.34	1.62	0.5
C10	805	—	1110	1.925	1.34	1.62	0.9
C8	2180	—	1750	1.54	1.39	1.73	1.5
C4	2420	—	1790	1.54	1.39	1.73	1.7
C2	2650	—	1830	1.54	1.39	1.73	1.9

<sup>a</sup> From Figure 11.

<sup>b</sup> From Brown et al.<sup>25</sup>



TABLE VII  
Configurational Data For HPC and HEC

Fraction	$\overline{DP}_z$	$M_z \times 10^3$	$(\overline{S^2})_z^{1/2}, \text{ \AA}$	$\alpha$	$(\overline{R^2})_z^{1/2}, \text{ \AA}$	$(\overline{R_0^2})_z^{1/2}, \text{ \AA}$	$(\overline{R_f^2})_z^{1/2}, \text{ \AA}$	$(\overline{R_0^2}/\overline{R_f^2})_z^{1/2}$
HPC in Ethanol								
D2	575	250	380 <sup>a</sup>	1.13	925	820	186	4.4
D3	888	370	445 <sup>a</sup>	1.14	1090	955	230	4.2
D4	1260	520	520 <sup>a</sup>	1.16	1275	1100	275	4.0
D5	1950	790	630 <sup>a</sup>	1.20	1550	1290	342	3.8
D6	4600	1840	935 <sup>a</sup>	1.26	2290	1820	525	3.5
HEC in Water <sup>b</sup>								
C11	455	112	305	1.04	745	715	170	4.2
C10	1075	265	450	1.06	1110	1045	255	4.1
C8	3040	720	715	1.06	1750	1650	430	3.8
C4	3370	765	730	1.07	1790	1670	450	3.7
C2	3670	840	750	1.08	1830	1690	470	3.6

<sup>a</sup> From Figure 11.

<sup>b</sup> From Brown et al.<sup>25</sup>

hindered random coil at high molecular weight to a relatively stiff rod at low DP.

The unperturbed root mean square end-to-end distance for 1,4'-poly-saccharide molecules, assuming free rotation of the chain units, may be calculated from<sup>33</sup>

$$(\overline{R_f^2})^{1/2} = 7.75 \overline{DP}^{1/2}.$$

The ratio of the corresponding actual unperturbed dimension,  $(\overline{R_0^2})^{1/2}$ , to this value is a measure of molecular chain stiffness. As is evident from an inspection of the data in the last column of Table VII, the configuration of HPC in ethanol is indistinguishable from that of HEC in water. In both systems  $(\overline{R_0^2}/\overline{R_f^2})^{1/2}$  decreases with increasing molecular weight, apparently approaching a limit of 3.5 or slightly less. This ratio is at the upper end of the range (2 to 3.5) which has been reported for other cellulose derivatives at high DP.<sup>34</sup> The rigidity of HPC molecules in solution is probably due, at least in part, to a relatively high order of intramolecular hydrogen bonding.<sup>35</sup> Such bonding also may be responsible for the extended configuration of HEC molecules in water, leading to the "anomalous" behavior previously described<sup>36</sup> for this polymer-solvent system.

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