A One-Point Intrinsic Viscosity Method for Hydroxyethylcellulose, Hydroxypropylcellulose, and Sodium Carboxymethylcellulose

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Synopsis

Statistical analysis of viscosity measurements on dilute solutions of hydroxyethylcellulose (HEC), hydroxypropylcellulose (HPC), and sodium carboxymethylcellulose (CMC) in the solvents water, 50/50 (v/v) water/ethanol, and $0.1M$ NaCl, respectively, demonstrated that the Martin equation,

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

fits experimental data better than the Huggins equation,

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

An average Martin k of 0.191 is applicable to a variety of HEC and HPC samples, including fractionated and unfractionated experimental and commercial preparations covering a wide range of substitution. In the case of a similar variety of CMC samples, an average k of 0.161 is characteristic.

Based on these k values and using the Martin equation in the form

$$\eta_{rel} = 1 + c[\eta]e^{2.303k[\eta]c}$$

tables were developed which permit direct reading of $[\eta]$ values corresponding to single η_{rel} measurements at concentrations of 0.05, 0.10, 0.20, or 0.50 g/dl. Intrinsic viscosities obtained in this fashion differ from those determined by the usual dilution multipoint technique on the same samples by an average of but 2%, at an estimated time saving of 50% or more. This degree of variation is no greater than that expected in routine measurements on duplicate solutions.

INTRODUCTION

Intrinsic viscosity $[\eta]$ is an important parameter in any detailed polymer characterization, and is of particular value in the estimation of average molecular weight. It is the limit of the quotient η_{sp}/c as c, the concentration (in grams per deciliter), approaches zero. The specific viscosity η_{sp} at a given temperature and concentration is obtained from the relation

$$\eta_{sp} = \frac{\eta_s - \eta_0}{\eta_0} = \eta_{rel} - 1$$

wherein η_s is the viscosity of the polymer solution, η_0 is the viscosity of the solvent used, and the ratio η_s/η_0 is the relative viscosity, η_{rel}.

Normally $[\eta]$ is determined by measuring η_{rel} at several concentrations, calculating the corresponding η_{sp} values, and then extrapolating the latter to zero concentration, using an appropriate relationship. It is apparent that considerable time and effort would be saved if $[\eta]$ could be determined directly from a single viscosity measurement at a known concentration. Numerous relationships have been developed which describe $[\eta]$ in terms of η_{sp} or η_{rel}. Among the more widely accepted of these are those attributed to Huggins,[1]

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

and Martin,[2]

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

Either of the above equations represents a potentially satisfactory instrument for a one-point $[\eta]$ determination, provided the appropriate k value is substantially constant over the solute viscosity and concentration ranges of interest.

In an earlier paper, Elliott et al.[3] demonstrated that the Martin equation fits experimental data for polyethylene and polypropylene in Decalin (decahydronaphthalene) at 135°C better than the Huggins equation. With the former in the form

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

universal graphs, applicable to any solute–solvent system, were constructed relating $k[\eta]c$ to $k\eta_{sp}$. If k is established experimentally, and η_{sp} is measured at a known concentration, $[\eta]$ may be calculated with the aid of these graphs with minimum effort.

The limitations of one-point $[\eta]$ equations derived by combining two empirical equations have been discussed earlier.[3] Previous investigation led to the conclusion that the most satisfactory one-point method is that based on an experimentally determined slope constant. This approach has been used in current studies, described herein, extending the application of the technique to three water-soluble cellulose ethers: hydroxyethylcellulose (HEC), hydroxypropylcellulose (HPC), and sodium carboxymethylcellulose (CMC).

EXPERIMENTAL

All measurements were made in a water bath at 25.00 ± 0.02°C using dilution Ubbelohde viscometers having flow times of approximately 100 sec for water. These viscometers had been calibrated with water and certified viscosity standards (available from the Cannon Instrument Co., P.O. Box 16, State College, Pa. 16801) by the method recommended in ASTM D445-53T. The kinetic energy correction was applied in all cases, but no shear rate corrections were made. Solutions were prepared at initial concentrations varying from 0.050 to 0.500 g/dl, depending on solution flow times, and then four dilutions were made to permit viscosity deter-

minations over a fivefold concentration range. Dilution was accomplished by pipetting into a fixed volume of original solution aliquots of previously temperature-conditioned solvent. A minimum of three replicate flow times were recorded for each sample at every dilution.

Samples of all three cellulose ethers included both fractionated and unfractionated commercial and experimental preparations. The 26 HEC's varied from M.S.[4] 1.6 to 2.9 in substitution, and from 1.6 to 16.9 in intrinsic viscosity. Water (containing 100 ppm of 4-chloro-3,5-xylenol as a biocide) was used as the solvent for this group.

Fourteen samples each of HPC and CMC were also used in this study. The solvent for the former was a 50/50 (v/v) mixture of ethanol and water (essentially identical intrinsic viscosities are obtained for HPC in ethanol, water, or the mixed solvent, see reference 5), while that for the latter was $0.1M$ sodium chloride. The HPC's varied from M.S. 3.4 to 4.6 in substitution, and from 0.9 to 12.4 in intrinsic viscosity. The CMC's ranged from 0.4 to 1.3 in D.S.[4] and from 1.8 to 16.0 in intrinsic viscosity.

Treatment of Data

General

A typical set of viscosity measurements on dilutions of a single HEC (sample E) solution is presented graphically in Figure 1, illustrating the application of both the Huggins and Martin equations. It is apparent that
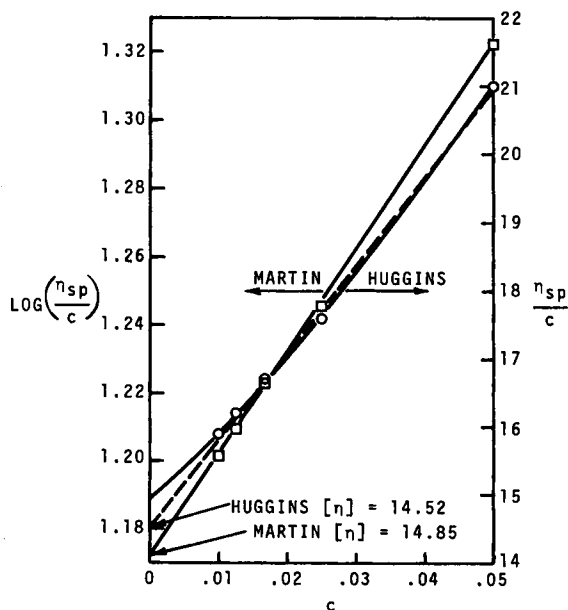

Fig. 1. Comparison of fit of Martin and Huggins equations to specific viscosity–concentration data for HEC sample E.

the least-squares Martin plot (solid line through square points) depicts a linear relationship, while the best representation of the same data with η_{sp}/c as a function of c is a curve (solid line through circular points). The least-squares (broken) line, based on the Huggins equation, is an appreciably poorer fit of the experimental data which indicates a lower intrinsic viscosity for this sample than that derived from the Martin plot. These findings duplicate those previously reported for polyethylene and polypropylene.[3]

In statistical terminology, the fit of the two equations to the experimental data was assessed in terms of the coefficient of variation, v. This quantity was calculated from the estimated standard deviation in $[\eta]$, $\hat{\sigma}[\eta]$, of the experimental values (representing viscosity measurements at the five concentrations investigated for each sample) from the least-squares line as follows:

$$v = \frac{100\hat{\sigma}[\eta]}{\text{indicated } [\eta]}.$$

In all cases, specific viscosity values were weighted in proportion to the difference between corrected flow times for the solution and solvent used in determining them. This procedure is justified on the basis of reduced measurement precision in the case of the dilutions of lower concentration, since $\eta_s \rightarrow \eta_0$ as $c \rightarrow 0$.

By means of this technique, it was demonstrated that the coefficient of variation resulting from use of the Martin equation was equal to or less than that derived from use of the Huggins equation for 46 of the 54 samples considered in this study. Accordingly, the development of a one-point intrinsic viscosity method was limited to application of the Martin relationship.

HEC Data

An analysis of experimental results on the 26 HEC samples is given in Table I. Intrinsic viscosities obtained from least-squares Martin plots are listed in column 7, while comparable data, derived from weighted η_{sp} measurements, are tabulated in column 8. The individual Martin constants determined in connection with the latter are given in column 11. The range of these values, 0.15 to 0.22, is so great that, at first thought, it appears hopeless to expect to obtain reliable intrinsic viscosities from a relationship predicated on the assumption of a constant k. (Undoubtedly some of the observed variation is the result of the heterogeneous nature of the samples considered—commercial and experimental preparations, both fractionated and unfractionated, covering a broad spectrum of substitution.) Additional reflection, however, suggests that appreciable variability in k would probably have only a minimal effect on $[\eta]$ deduced from η_{sp}/c via the Martin equation, and this has been shown to be the case.[3]

If each individual k value (column 11) is weighted inversely in proportion to the variance associated with it, an overall average k for the 26 HEC

TABLE I HEC—Analysis of Intrinsic Viscosity Data (Solvent–Water)

| Sample (1) | Type[a] (2) | M.S. (3) | Initial conc., c, g./dl. (4) | η_{rel} (5) | η_{sp}/c (6) | $[\eta]$ from Martin plot (7) | Determined from weighted viscosity measurements by use of Martin equation | | | | | | $[\eta]$ from η_{rel} assuming k = 0.194 (14) | From $[\eta]$-vs.-η_{rel} tables assuming k = 0.191 | | |
							$[\eta]$ (8)	$\partial[\eta]$ (9)	$\dfrac{100\,\partial[\eta]}{[\eta]}$ (10)	k (11)	∂k (12)	$100\partial k/k$ (13)		$[\eta]$ (15)	Deviation from multi-point value (16)	Percentage deviation (17)
A	F	2.89	0.050	2.236	24.7	17.0	16.870	0.351	2.08	0.196	0.0179	9.13	16.93	17.01	+0.14	0.83
B	F	2.51	0.050	2.174	23.5	16.2	16.241	0.153	0.94	0.197	0.0084	4.26	16.31	16.38	+0.14	0.86
C	U	2.68	0.050	2.144	22.9	15.6	15.616	0.250	1.60	0.212	0.0149	7.03	16.00	16.07	+0.45	2.88
D	F	2.55	0.050	2.109	22.2	15.5	15.483	0.136	0.88	0.202	0.0081	4.00	15.64	15.70	+0.22	1.42
E	F	2.44	0.050	2.051	21.0	14.8	14.852	0.133	0.90	0.203	0.0086	4.24	15.02	15.09	+0.24	1.62
F	U	2.42	0.050	1.953	19.1	14.2	14.192	0.083	0.59	0.181	0.0058	3.20	13.96	14.01	-0.18	1.27
G	F	2.27	0.050	1.991	19.8	14.3	14.148	0.136	0.96	0.206	0.0096	4.66	14.38	14.43	+0.28	1.98
H	U	1.90	0.050	1.959	19.2	14.0	13.999	0.144	1.03	0.195	0.0103	5.28	14.02	14.08	+0.09	0.64
I	U	2.45	0.050	1.999	20.0	13.9	13.950	0.354	2.54	0.223	0.0261	11.7	14.47	14.52	+0.57	4.11
J	U	2.59	0.050	1.866	17.3	13.0	13.026	0.205	1.57	0.190	0.0168	8.85	12.97	13.01	-0.02	0.15
K	F	2.46	0.050	1.847	17.0	12.8	12.745	0.111	0.87	0.194	0.0095	4.90	12.74	12.79	+0.04	0.31
L	U	2.54	0.050	1.728	14.6	11.6	11.662	0.260	2.23	0.164	0.0257	15.6	11.31	11.35	-0.31	2.66
M	F	2.50	0.050	1.568	11.35	9.3	9.281	0.157	1.69	0.189	0.0244	12.9	9.24	9.26	-0.02	0.22
N	U	1.90	0.050	1.570	11.41	9.2	9.162	0.048	0.50	0.208	0.0076	3.66	9.27	9.29	+0.13	1.46
O	F	2.48	0.100	2.320	13.2	8.9	8.850	0.053	0.60	0.196	0.0050	2.55	8.88	8.92	+0.07	0.79
P	F	2.68	0.100	2.023	10.2	7.4	7.423	0.053	0.72	0.188	0.0068	3.62	7.36	7.39	-0.03	0.40
Q	F	1.65	0.100	1.817	8.17	6.1	6.091	0.079	1.30	0.210	0.0149	7.10	6.20	6.22	+0.13	2.14
R	F	2.64	0.100	1.728	7.28	5.8	5.796	0.069	1.19	0.171	0.0139	8.13	5.66	5.68	-0.12	2.07
S	F	1.64	0.100	1.690	6.90	5.6	5.570	0.073	1.31	0.167	0.0159	9.52	5.42	5.43	-0.14	2.51
T	F	2.63	0.100	1.654	6.54	5.2	5.186	0.111	2.14	0.193	0.0279	14.5	5.19	5.20	+0.01	0.19
U	F	1.76	0.100	1.535	5.35	4.38	4.365	0.047	1.08	0.203	0.0165	8.12	4.40	4.41	+0.04	0.92
V	U	2.57	0.100	1.423	4.23	3.70	3.712	0.081	2.18	0.150	0.0376	25.1	3.60	3.61	-0.10	2.70
W	F	1.83	0.100	1.426	4.26	3.70	3.663	0.111	3.03	0.178	0.0539	30.3	3.62	3.63	-0.03	0.82
X	F	2.61	0.200	1.773	3.86	2.98	2.978	0.016	0.54	0.190	0.0062	3.2	2.97	2.98	0.00	0.00
Y	F	1.80	0.200	1.617	3.09	2.52	2.551	0.044	1.73	0.161	0.0224	13.9	2.47	2.48	-0.07	2.74
Z	F	2.57	0.200	1.370	1.85	1.65	1.637	0.060	3.68	0.162	0.0713	44.0	1.60	1.61	-0.03	1.83
(Weighted) Av.										(0.194)						1.44

[a] F = Fraction; U = unfractionated.

TABLE II
HPC—Analysis of Intrinsic Viscosity Data (Solvent—50:50 Water:Ethanol)

Sample (1)	Type[a] (2)	M.S. (3)	Initial conc. c, g./dl (4)	η_{rel} (5)	η_{sp}/c (6)	[η] from Martin plot (7)	Determined from weighted viscosity measurements by use of Martin equation [η] (8)	∂[η] (9)	100 ∂[η]/[η] (10)	k (11)	∂k (12)	100 ∂k/k (13)	[η] from η_{rel} assuming k = 0.188 (14)	From [η]-vs.-η_{rel} tables assuming k = 0.191 [η] (15)	Deviation from multipoint value (16)	Percentage deviation (17)
A	U	4.6	0.100	3.229	22.29	12.4	12.382	0.144	1.16	0.207	0.0080	3.86	12.80	12.73	+0.35	2.83
B	U	4.2	0.100	2.920	19.20	11.3	11.175	0.074	0.66	0.213	0.0050	2.34	11.61	11.55	+0.47	4.20
C	U	4.1	0.100	2.518	15.18	9.9	9.859	0.126	1.28	0.190	0.0103	5.42	9.89	9.85	-0.01	0.10
D	F	3.6	0.200	4.706	18.53	8.47	8.496	0.074	0.87	0.199	0.0046	2.31	8.71	8.65	+0.15	1.77
E	F	3.6	0.200	3.536	12.68	6.83	6.861	0.077	1.12	0.195	0.0069	3.54	6.95	6.91	+0.05	0.73
F	F	3.6	0.200	2.938	9.69	5.85	5.836	0.067	1.15	0.189	0.0080	4.23	5.84	5.81	-0.03	0.52
G	F	3.7	0.200	2.548	7.74	5.10	5.086	0.047	0.93	0.180	0.0070	3.89	5.01	4.99	-0.09	1.77
H	U	3.7	0.200	2.256	6.28	4.30	4.304	0.036	0.84	0.190	0.0075	3.95	4.32	4.30	0.00	0.00
I	U	3.7	0.200	2.182	5.91	4.23	4.214	0.085	2.02	0.173	0.0185	10.7	4.13	4.12	-0.09	2.14
J	F	3.8	0.200	3.150	4.30	2.60	2.610	0.046	1.76	0.163	0.0238	14.6	2.51	2.49	-0.12	4.60
K	U	3.4	0.500	2.235	2.47	1.76	1.776	0.037	2.08	0.157	0.0181	11.5	1.71	1.70	-0.08	4.50
L	U	3.8	0.500	1.930	1.86	1.45	1.438	0.006	0.42	0.156	0.0044	2.82	1.38	1.37	-0.07	4.87
M	U	3.5	0.500	1.595	1.19	1.01	1.004	0.019	1.89	0.148	0.0224	15.1	0.97	0.96	-0.04	3.98
N	F	4.3	0.500	1.540	1.08	0.92	0.928	0.066	7.11	0.149	0.2280	153.	0.89	0.89	-0.04	4.31
(Weighted) Av.										(0.188)						2.59

[a] F = Fraction; U = unfractionated.

samples is obtained (k = 0.194). This average Martin k can then be used as a basis for estimating $[\eta]$ from η_{sp}/c at the highest concentration considered for each sample. Such estimates for the entire series are listed in column 14 of Table I.

HPC Data

Experimental data on the 14 HPC samples are analyzed in Table II, using the techniques previously described for HEC. The weighted average k for HPC (column 11) is 0.188, only 0.006 lower than that for HEC. If a grand average Martin k of 0.191 is considered applicable to both of these cellulose ethers, the one-point $[\eta]$ values listed in column 15 of Tables I and II are obtained. These estimated intrinsic viscosities differ only insignificantly from those (column 14) resulting from use of the more appropriate k's specific to the individual cellulose ethers.

CMC Data

Analysis of the CMC intrinsic viscosity data, Table III, was handled in the same fashion as that for the two other cellulose ethers previously discussed. The solvent for the polyelectrolyte samples, however, was $0.1M$ NaCl. As would be expected, the weighted average Martin k for this group, 0.161, is appreciably different from those characteristic of the non-electrolytes. It is recognized that this value is not only descriptive of CMC, but is also a function of the ionic strength of the medium in which viscosity measurements were made.

The One-Point $[\eta]$ Method

The appropriate amount of cellulose ether (corrected for moisture content) is carefully weighed into a 100-ml volumetric flask. Approximately 50 ml of the proper solvent (see experimental section of this paper) is added, and the mixture is agitated on a mechanical shaker until dissolution is complete. The flask is then placed in a 25°C water bath, and, after temperature equilibrium is established, the solution is diluted to its final volume with previously temperature-conditioned solvent.

The flow times of the solution and of the solvent are determined in a suitable viscometer, kinetic energy corrections being applied. The ratio of these corrected flow times is the relative viscosity of the solution since, at the concentration levels considered, the density of the solution is approximately equal to that of the solvent. The value of $[\eta]$ is then read directly from the appropriate table for the particular cellulose ether and concentration involved, using linear interpolation. These tables (copies of these tables and/or the universal graphs mentioned earlier in the text are available to interested parties on request) are based on the Martin equation (with k equal to 0.191 or 0.161) which may be written in the form

$$\eta_{rel} = 1 + c[\eta]e^{2.303k[\eta]c}.$$

TABLE III
CMC—Analysis of Intrinsic Viscosity Data (Solvent—0.1M NaCl)

Sample (1)	Type[a] (2)	D.S. (3)	Initial conc. c, g/dl (4)	η_{rel} (5)	η_{sp}/c (6)	$[\eta]$ from Martin plot (7)	Determined from weighted viscosity measurements by use of Martin equation						From $[\eta]$-vs.-η_{rel} tables assuming $k = 0.161$		
							$[\eta]$ (8)	$\partial[\eta]$ (9)	$\dfrac{100\,\partial[\eta]}{[\eta]}$ (10)	k (11)	∂k (12)	$\dfrac{100\,\partial k}{k}$ (13)	$[\eta]$ (14)	Deviation from multipoint value (15)	Percentage deviation (16)
A	U	0.80	0.050	2.060	21.2	16.0	15.976	0.180	1.13	0.153	0.0098	6.40	15.81	−0.17	1.06
B	F	0.41	0.050	2.030	20.6	14.9	14.793	0.097	0.66	0.195	0.0063	3.23	15.47	+0.68	4.60
C	U	0.77	0.050	1.950	19.0	14.1	14.000	0.124	0.89	0.190	0.0089	4.68	14.51	+0.51	3.64
D	F	0.42	0.050	1.705	14.1	11.3	11.267	0.038	0.34	0.173	0.0022	1.27	11.41	+0.14	1.24
E	U	0.41	0.050	1.645	12.9	10.4	10.439	0.076	0.73	0.177	0.0093	5.25	10.60	+0.16	1.53
F	U	0.76	0.100	2.233	12.5	8.8	8.813	0.044	0.50	0.169	0.0075	4.44	8.87	+0.06	0.68
G	F	1.23	0.100	2.070	10.67	8.2	8.344	0.150	1.80	0.122	0.0082	6.72	7.96	−0.38	4.56
H	U	1.25	0.100	1.820	8.20	6.6	6.621	0.017	0.26	0.140	0.0025	1.79	6.46	−0.16	2.42
I	U	0.94	0.100	1.740	7.39	6.15	6.122	0.063	1.03	0.133	0.0110	8.27	5.94	−0.18	2.94
J	U	0.80	0.100	1.671	6.71	5.47	5.479	0.033	0.60	0.160	0.0074	4.62	5.48	0.00	0.00
K	U	1.27	0.200	2.286	6.43	4.47	4.461	0.029	0.65	0.178	0.0053	2.98	4.58	+0.12	2.69
L	F	1.24	0.200	1.890	4.45	3.53	3.524	0.024	0.68	0.144	0.0068	4.72	3.45	−0.07	1.99
M	U	0.79	0.200	1.620	3.10	2.58	2.586	0.040	1.55	0.154	0.0199	12.9	2.56	−0.03	1.16
N	F	1.27	0.200	1.414	2.07	1.80	1.809	0.014	0.77	0.162	0.0143	8.82	1.81	0.00	0.00
(Weighted) Av.									0.77	(0.161)					2.04

[a] F = Fraction; U = unfractionated.

Although 0.100 g/dl is preferred, the concentration of high $[\eta]$ samples may be either 0.050 or 0.100 g/dl, while that of low $[\eta]$ samples may be either 0.200 or 0.500 g/dl. Tables were developed to cover all of these possibilities. Best results are obtained when η_{rel} is maintained within the limits 1.4 to 5.

RESULTS AND DISCUSSION

The one-point intrinsic viscosities (Tables I and II, column 15; and Table III, column 14) for the 54 cellulose ethers studied in this investigation differ from the values (Tables I, II, and III, column 8) determined by the weighted, multipoint technique by an average of approximately 2% (Tables I, II, and III, last column). This degree of variability is the same order of magnitude as that which might be expected between routine measurements on duplicate solutions. Accordingly, the simplified method appears to be satisfactory for all except the most exacting type of work. A bonus for its use is realized in the form of a time saving of greater than 50%. This method has been in use in Hercules laboratories for several years and has proved to be eminently satisfactory.

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