

A One-Point Intrinsic Viscosity Method for Polyethylene and Polypropylene

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Synopsis

A statistical analysis of dilute solution viscosity data for a wide range of polyethylene and polypropylene samples in Decalin at 135°C has shown that the Martin equation

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

fits the experimental data better than the Huggins equation

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

at higher values of $[\eta]c$. A grand average k of 0.139 is applicable to both polymers. Based upon this, tables have been calculated permitting the ready determination of $[\eta]$ from a single relative viscosity measurement at a known concentration. The Martin equation has been put into a universal form, permitting $[\eta]$ to be calculated from a measured η_{sp} if k and c are known. Graphs relating η_{sp} to $[\eta]$ are included for use of the Martin equation over wide ranges of both k and c . It was found that the Solomon and Ciuta equation

$$[\eta]c = (2\eta_{sp} - 2 \ln \eta_{rel})^{1/2}$$

fits the experimental polyethylene and polypropylene data, and the reasons for this are discussed.

INTRODUCTION

The intrinsic viscosity, $[\eta]$, is probably the most frequently measured property of high polymers. It is relatively easy to determine, provides an estimate of molecular weight, and is an essential parameter in any detailed polymer characterization.¹ It is generally determined by measuring the relative viscosities, η_{rel} , of a series of solutions of differing concentration. From these data η_{sp}/c is calculated, where η_{sp} is the specific viscosity and c is the polymer concentration (in g/dl). The η_{sp}/c values are then extrapolated to zero concentration, using an appropriate relationship, to obtain $[\eta]$.

It is apparent that considerable time and effort would be saved if, instead of determining η_{rel} for a series of solutions, a single determination at a known concentration might be used to give $[\eta]$ directly. Some years ago, Martin² proposed a method for the determination of the intrinsic viscosity of cellulose in cuprammonium or 0.5*M* cupriethylenediamine based upon a single

viscosity measurement. Recently a number of workers have proposed and discussed various equations for obtaining $[\eta]$ from a single determination of η_{rel} . These include Solomon and Ciuta,³ Palit and Kar,⁴ and Deb and Chatterjee.⁵ The current interest in one-point $[\eta]$ methods has prompted us to describe the one-point method for polyethylene and polypropylene which has been in use in our laboratories for the past five years, together with the experimental data and statistical analyses upon which it is based.

EXPERIMENTAL

Measurements were made on a wide variety of commercial and experimental samples of polyethylene and polypropylene. The ratio \bar{M}_w/\bar{M}_n was determined by gel permeation chromatography. ASTM Method 1238-62T was used to measure i_2 at 190°C. The samples are described in Tables I and II.

Decalin (decahydronaphthalene) was du Pont technical grade. In certain cases, the Decalin was percolated through silica gel and then distilled.⁶ Substantially the same results were obtained using the Decalin as received and after purification. Two grams of phenyl- β -naphthylamine per kilogram of Decalin was added as an antioxidant.

Dilution Ubbelohde viscometers⁷ having flow times of approximately 100 sec for water at 25°C were used. These were calibrated with water and standard oils from the National Bureau of Standards according to ASTM Method D445-53T. The kinetic energy correction was applied in all cases. Measurements were made in a constant temperature oil bath at 135 \pm 0.1°C.

Decalin was found to have a density of 0.883 g/ml at 25°C and 0.801 g/ml at 135°C. Thus, for practical routine use (error 0.5%), 0.90 ml of Decalin at 25°C is equivalent to 1.00 ml at 135°C. Solutions of the polymers were prepared on a weight basis, and the weight of the solution introduced into the viscometer was determined. The volume of the solution at 135°C and its concentration in g/dl at this temperature were calculated using the densities given above. Dilutions were made by pipetting Decalin into the viscometer and again correcting the added volume to the operating temperature. At least four dilutions were made in each $[\eta]$ determination.

TREATMENT OF DATA

Viscosity-Concentration Relationships

In order to obtain the $[\eta]$ of a polymer from a series of viscosity measurements, it is necessary to assume some functional relationship between relative viscosity and concentration. Numerous relationships have been proposed, and these have been thoroughly reviewed by Rutgers.⁸ Of these many relationships, the Huggins equation

$$\eta_{sp}/c = [\eta] + k'[\eta]^2c \quad (1)$$

and the Martin equation

$$\log(\eta_{sp}/c) = \log[\eta] + k[\eta]c \quad (2)$$

have proved to be among the most useful. The experimental data were treated in terms of each of these equations.

Effect of Shear Rate

It has been found that solutions of polyethylene and polypropylene in Decalin exhibit non-Newtonian behavior, even at the low concentrations normally used in the determination of $[\eta]$. A study of the effect of shear rate on η_{sp} was carried out in this laboratory,⁹ using a variable shear Wagner-Russell capillary viscometer.¹⁰ The effect of shear rate for both polymers could be described by the following empirical equation:

$$\eta_{sp\dot{\gamma}=0} = \eta_{sp}(1 + 1.5 \times 10^{-4} \eta_{sp}\dot{\gamma}) \quad (3)$$

where $\eta_{sp\dot{\gamma}=0}$ is the specific viscosity at zero shear rate and η_{sp} is the specific viscosity at the shear rate, $\dot{\gamma}$.

Almost all theories of the effect of shear rate on dilute solution viscosity predict a second-power dependence on $\dot{\gamma}$ for the initial non-Newtonian portion of this $\eta_{sp}-\dot{\gamma}$ curve.¹¹ Cases have been reported, however, where a linear shear rate dependence describes the experimental data.^{11,12} Inasmuch as our experimental data follow eq. (3), it is clear that any shear rate correction disappears as η_{sp} (or the concentration) approaches zero. Thus, the extrapolation to zero concentration, which is necessary in using either the Martin or Huggins equations, results in the elimination of any necessity for a shear rate correction.

Statistical Treatment of Data

To obtain an objective estimate of $[\eta]$ and the slope constants k' and k , the experimental data were fitted to the Huggins and Martin equations by the method of least squares. Before this was done, it was necessary to decide whether or not to weight the experimental points and, if so, in what way. As the concentration in a given set of measurements becomes lower, the precision in η_{sp} becomes less, inasmuch as the viscosity of the solution approaches that of the solvent and η_{sp} becomes the relatively small difference between two large numbers. Based upon this consideration, each point was weighted by a factor equal to the difference between the flow times of the solution and solvent, both corrected for kinetic energy.

Least-square values of $[\eta]$ and the slope constants for both the Martin and Huggins equations are given in Tables I and II.

Estimates of the coefficients of variation (e.g., $100 \hat{\sigma}[\eta]/[\eta]$) are included for these quantities, $\hat{\sigma}[\eta]$ being the estimate of the standard deviation in $[\eta]$.

Consideration of these coefficients of variation for the more extensive polyethylene $[\eta]$ results indicate that Martin's equation fits the experi-

TABLE I. Polyethylene—Analysis of Intrinsic Viscosity Data

Sample	i_2 at 190°C	Remarks	Initial concn., (g./dl)	$[\eta]$ from Martin plot	Calculated by Martin equation			Calculated by Huggins equation				
					$[\eta]$	k	$100\phi/k$	$[\eta]$	$100\phi/[\eta]$	k'/k'		
A	0.100	linear	0.100	19.7	19.81	0.46	0.1320	1.44	18.19	1.17	0.5423	1.92
B	0.100	linear	0.100	26.9	26.91	0.80	0.1434	1.88	21.34	5.57	0.9660	6.47
C	0.200	linear, $\bar{M}_w/\bar{M}_n \sim 35$	0.200	2.10	2.185	0.68	0.1982	5.30	2.169	0.74	0.5292	4.41
	0.500		0.500	2.33	2.343	1.14	0.1373	5.18	2.277	1.68	0.4302	4.79
	0.500		0.500	2.15	2.155	0.49	0.1672	2.03	2.077	1.15	0.5491	2.81
D	0.300	\bar{M}_w/\bar{M}_n very high	0.300	4.00	4.059	1.34	0.1756	4.84	3.855	0.92	0.6233	1.86
	0.500		0.500	4.50	4.480	0.80	0.1315	2.28	4.013	0.90	0.5967	1.26
	0.500 ^a		0.500 ^a	4.59	4.594	1.33	0.1525	3.69	4.081	0.91	0.6201	1.24
E	0.27		0.500	1.93	1.927	0.36	0.1502	1.80	1.884	0.71	0.4529	2.30
	0.500 ^a		0.500 ^a	1.96	1.962	0.50	0.1379	2.68	1.925	0.77	0.4068	2.70
F	~5		0.300	2.32	2.327	0.51	0.1721	2.96	2.293	0.65	0.4919	2.64
G	0.50	linear, $\bar{M}_w/\bar{M}_n = 15$	0.500	2.36	2.347	0.35	0.1471	1.43	2.266	0.81	0.4775	2.01
H	0.45	$\bar{M}_w/\bar{M}_n = 5.6$	0.500	2.33	2.267	2.16	0.1574	9.01	2.189	2.62	0.5125	6.50
	0.500		0.500	2.35	2.323	0.62	0.1378	2.83	2.260	0.86	0.4300	2.46
	0.500 ^a		0.500 ^a	2.36	2.357	0.55	0.1304	2.60	2.298	0.81	0.4008	2.42
I	0.500	$\bar{M}_w/\bar{M}_n = 4.9$	0.500	1.91	1.939	0.96	0.1615	4.45	1.889	0.97	0.4988	2.83
	0.800		0.800	1.99	1.980	0.74	0.1413	2.54	1.866	1.77	0.5196	3.33
	0.800 ^a		0.800 ^a	2.13	2.145	0.82	0.1267	2.92	2.030	1.90	0.4570	3.70
J	0.50	long-chain branched	0.500	1.56	1.562	0.48	0.1608	2.74	1.536	0.56	0.4645	2.14
K	0.75		0.500	1.95	2.064	5.72	0.1113	34.6	2.039	6.64	0.3134	2.87
	0.800		0.800	1.89	1.898	0.91	0.1471	3.19	1.790	1.15	0.5387	2.14
	0.800 ^a		0.800 ^a	1.86	1.865	0.36	0.1451	1.31	1.768	1.17	0.5194	2.25
L	0.60	short-chain branched, narrow dist.	0.500	2.06	2.039	0.48	0.1730	2.02	1.969	0.87	0.5615	2.07
	0.800		0.800	2.00	1.998	0.31	0.1419	1.06	1.878	1.34	0.5269	2.47
	0.800 ^a		0.800 ^a	2.01	2.007	0.36	0.1496	1.20	1.874	0.81	0.5739	1.38
M	0.500	linear, $\bar{M}_w/\bar{M}_n = 2.4$	0.500	0.67	0.678	1.90	0.1008	35.5	0.677	1.99	0.2453	33.2
	1.500		1.500	0.65	0.657	0.79	0.1361	4.25	0.644	1.23	0.4020	4.08
	1.500 ^a		1.500 ^a	0.74	0.746	0.60	0.1520	2.56	0.724	1.09	0.4843	2.66

av. 0.14635

^a Distilled Decalin used.

TABLE II
 Polypropylene—Analysis of Intrinsic Viscosity Data

Sample	i_2 at 230°C.	Remarks	Initial concn. (g/dl)	$[\eta]$ from Martin plot	Calculated by Martin equation			Calculated by Huggins equation				
					$[\eta]$	$100\phi [\eta]/[\eta]$	k	$100\phi/k$	$[\eta]$	$100\phi [\eta]/[\eta]$	k'	$100\phi/k'$
N		exptl. high mol wt.	0.100	12.0	12.10	1.40	0.1483	5.80	11.69	1.09	0.4816	2.80
O	6.0		0.500	1.42	1.429	6.79	0.1368	4.75	1.415	0.81	0.3737	4.20
P	0.3		0.200	8.48	8.540	0.81	0.1343	2.75	8.026	0.70	0.5001	1.32
Q		exptl. broad dist.	0.300	3.05	3.082	0.92	0.1601	4.50	3.013	0.87	0.4843	2.75
			0.500	3.09	3.078	1.27	0.1294	4.86	2.945	0.88	0.4422	1.95
			0.500*	3.28	3.294	1.11	0.1205	4.23	3.157	0.68	0.4097	1.51
R	3.0		0.500	2.31	2.324	1.09	0.1206	5.55	2.278	0.99	0.3582	3.26
			0.800	2.36	2.348	0.79	0.1086	2.94	2.239	0.31	0.3767	0.66
			0.800*	2.47	2.488	0.55	0.1100	1.91	2.355	0.44	0.3962	0.86
S		Exptl. degraded	0.499	1.71	1.702	0.36	0.1372	2.18	1.679	0.33	0.3887	1.36
T	4.7		0.500	2.23	2.239	0.72	0.1558	3.08	2.164	1.44	0.5044	3.54
			0.500	2.35	2.341	0.44	0.1188	2.19	2.294	0.40	0.3529	1.36
							av. 0.1317					

* Distilled Decalin used.

mental data better than Huggins's. The situation appears to be reversed in the polypropylene case. However, these polymer samples were fewer in number and predominantly in the lower $[\eta]$ range. Here, both equations fit the experimental points quite well, and it is difficult to make a choice. Hence, the Martin equation, which shows a better fit at higher $[\eta]$ values, was selected as the basis of the one-point $[\eta]$ method.

This choice is confirmed in a more subjective manner when plots of the experimental data for a very high $[\eta]$ polymer, sample B, are made using both relationships. Admittedly, the $[\eta]$ of this sample is unusually high, but it illustrates the better fit of the Martin equation. This is shown in Figure 1. It should be noted that the observed slope constant k is 0.143, in

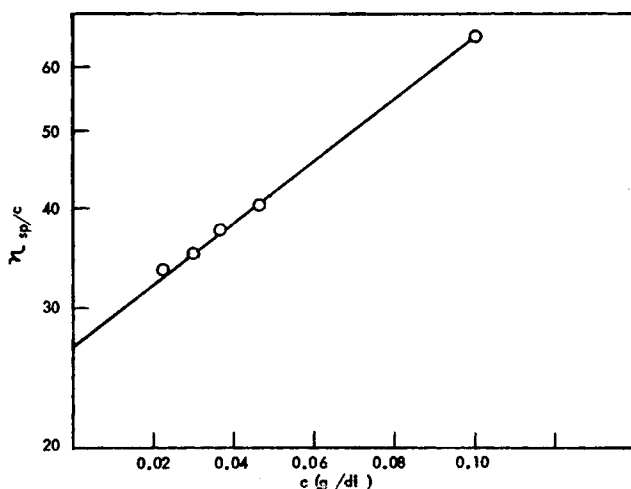


Fig. 1. Martin plot for polyethylene, sample B: $[\eta]$ by least squares, 26.9; $[\eta]$ from highest point using $k = 0.139$, 27.3.

close agreement with 0.139, the grand average of both polymers. In contrast, there is marked curvature in the deviation of the experimental points from the least-squares Huggins line, shown in Figure 2. In addition, the slope constant k' for this line is approximately twice as high as any other in either series of polymers studied.

Consideration of Tables I and II makes it quite clear that treatment of the data by the Huggins equation tends to yield lower values than those obtained using the Martin equation. This, in itself, is not a matter of great consequence. The important point is that, by both objective statistical analysis and the more subjective plotting of points, the Martin equation appears to describe experimental data better over a wider range of $[\eta]$ and c .

Interestingly, Sakai¹³ has analyzed extrapolation procedures for $[\eta]$ and has proposed using averages from Martin and Huggins plots for measurements in good solvents. This procedure, however, does not lend itself to a one-point $[\eta]$ method.

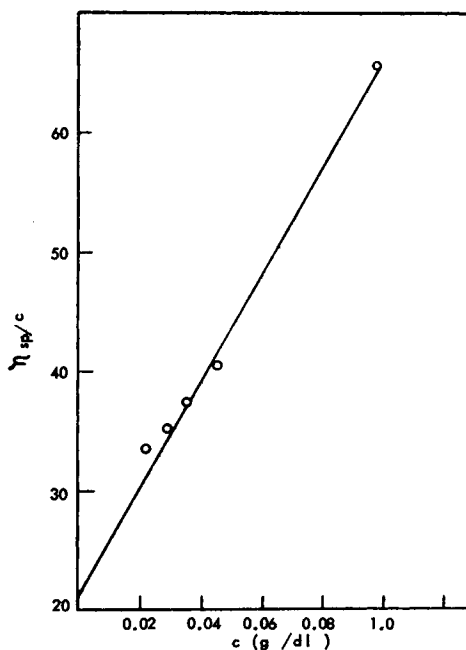


Fig. 2. Huggins plot for polyethylene, sample B: $[\eta]$ from least-squares line, 21.3.

At first glance, the spread of k values between samples and even between duplicate determinations on the same sample seems to be so large that the use of eq. (2) as the basis for a one-point $[\eta]$ method appears unpromising. It has long been known, however, that to achieve very good precision and accuracy in the experimental determination of the slope constant requires extraordinarily precise measurement techniques. Extensive studies¹⁴ have shown, however, that for a given polymer-solvent system at a fixed temperature, k is a constant. Any appreciable variation in k indicates that the polymer is not the "given polymer" and that some chemical or structural difference is present. These differences may be rather subtle; in the case of cellulose derivatives, for example, variations in the degree and uniformity of substitution or the presence of traces of bound ions may be responsible. In cases such as this, where the effect of association at finite concentration can be reduced by extrapolation to zero concentration, we have found it preferable to use a solvent that minimizes association and allows the use of the one-point method.

Some years ago, however, Davis¹⁵ carried out a very thorough analysis of capillary viscometry and of the determination of $[\eta]$ by a one-point method, based on the theory of the propagation of errors. Based upon reasonable assumptions, he concluded, that, if k is known to only $\pm 40\%$, $[\eta]$ can be determined to $\pm 2\%$ if the concentration at which the viscosity is measured is such that $[\eta]c \leq 0.1$. This is too low, in general, for a standardized method of wide applicability, but it does indicate that reasonable preci-

TABLE III
 Polyethylene—One-Point Intrinsic Viscosity*

Sample	[η] from least squares	[η] from exptl. point nearest $c = 0.100$			[η] from exptl. point nearest $c = 0.500$		
		$k =$	$k =$	$k =$	$k =$	$k =$	$k =$
		0.146	0.132	0.139	0.146	0.132	0.139
A	19.8	19.0	19.8	19.4	—	—	—
B	26.9	26.7	28.0	27.3	—	—	—
C	2.19	2.23	2.24	2.23	—	—	—
	2.34	2.33	2.34	2.34	2.30	2.37	2.34
	2.16	2.20	2.22	2.21	2.24	2.30	2.27
D	4.06	4.21	4.27	4.24	—	—	—
	4.48	4.37	4.43	4.40	4.28	4.47	4.38
	4.59	4.43	4.49	4.46	4.40	4.60	4.50
E	1.93	1.94	1.95	1.94	1.94	1.99	1.96
	1.96	1.95	1.96	1.96	1.93	1.98	1.96
F	2.33	2.34	2.35	2.35	—	—	—
G	2.35	2.34	2.37	2.36	2.35	2.42	2.38
H	2.27	2.30	2.32	2.31	2.31	2.38	2.35
	2.32	2.32	2.33	2.32	2.29	2.35	2.32
	2.36	2.36	2.38	2.37	2.28	2.35	2.32
I	1.94	1.92	1.94	1.93	1.99	2.04	2.01
	1.98	1.99	2.01	2.00	1.96	2.00	1.98
	2.15	2.15	2.17	2.16	2.07	2.12	2.09
J	1.56	1.56	1.57	1.57	1.59	1.63	1.61
K	2.06	2.26	2.28	2.27	1.95	2.00	1.97
	1.90	1.87	1.89	1.88	1.90	1.94	1.92
	1.87	1.87	1.89	1.88	1.86	1.89	1.88
L	2.04	2.06	2.07	2.07	2.14	2.19	2.16
	2.00	1.99	2.01	2.00	1.98	2.02	2.00
	2.01	2.00	2.02	2.01	2.02	2.06	2.04
M	0.68	0.70	0.70	0.70	0.66	0.66	0.66
	0.66	0.66	0.67	0.66	0.65	0.66	0.66
	0.75	0.75	0.76	0.76	0.74	0.75	0.75

* Units, dl/g.

sion in $[\eta]$ can be achieved with a one-point method, even if there is considerable uncertainty in the value of k .

Examination of the data in Tables I and II does not reveal any correlation between k and the known chemical composition, molecular weight, or molecular weight distribution of the sample. In a series of $[\eta]$ measurements for a number of samples of the same type of polymer, using the usual multipoint method, an apparently wide spread of the slope constant k will usually be found. This variation in k will then introduce some, albeit relatively small, error in the extrapolated $[\eta]$ values. We believe that the use of an average k value, established by using a wide range of samples, together with an experimental η_{rel} value determined at a concentration where good precision can be expected, will yield a more accurate estimate of $[\eta]$ than that obtained from a multipoint measurement.

TABLE IV
Polypropylene—One-Point Intrinsic Viscosity*

Sample	[η] from least squares	[η] from exptl. point nearest $c = 0.100$			[η] from exptl. point nearest $c = 0.500$		
		$k =$	$k =$	$k =$	$k =$	$k =$	$k =$
		0.146	0.132	0.139	0.146	0.132	0.139
N	12.1	12.1	12.5	12.3	—	—	—
O	1.43	1.44	1.45	1.45	1.41	1.44	1.42
P	8.54	8.42	8.60	8.51	—	—	—
Q	3.08	3.08	3.11	3.09	—	—	—
	3.08	2.98	3.01	3.00	2.95	3.06	3.00
	3.29	3.18	3.22	3.20	3.09	3.20	3.14
R	2.32	2.27	2.29	2.28	2.21	2.27	2.24
	2.35	2.25	2.28	2.26	2.23	2.28	2.25
	2.49	2.39	2.42	2.41	2.36	2.41	2.39
S	1.70	1.69	1.70	1.69	1.68	1.72	1.70
T	2.24	2.27	2.29	2.28	2.28	2.35	2.31
	2.34	2.28	2.30	2.29	2.21	2.28	2.25

* Units, dl/g.

The average k for polyethylene is 0.146, while that for polypropylene is 0.132. This difference is considerably smaller than that between and within samples of the same polymer; hence a grand average value of 0.139 was selected for use.

Tables III and IV compare the [η] of the various samples calculated from η_{rel} at the indicated concentrations, using k values of 0.132, 0.139, and 0.146, with that obtained by the least-squares treatment of at least five experimental points discussed earlier. Differences between [η] for the various values of k are smaller than variations observed in replicate determinations by the five-point method. This confirms our earlier conclusions that, for a given polymer-solvent system, [η] determined from one measurement of relative viscosity using an average k value obtained from many measurements is, in general, more accurate than [η] determined using the conventional four- or five-point procedure.

Figures 1 and 3 illustrate how well the one-point method fits the experimental data. In Figure 1, the [η] obtained by using the highest point and the value of 0.139 for k is 27.3, compared with 26.9 from the least-squares line. Figure 3 illustrates the fact that even when the fit to the points is seemingly bad and k is unusually far from the average, the value of the one-point [η] is in acceptable agreement with the five-point method. The least-squares line gave [η] = 2.33 with $k = 0.172$ for sample F, while the one-point method using $k = 0.139$ gives 2.43.

OUTLINE OF THE [η] METHOD

The sample of polyethylene or polypropylene is accurately weighed into a volumetric flask. Based upon this weight, the volume of solution at 135°C

TABLE V
Relationship Between η_{rel} and $[\eta]$ for $c = 0.100$ g/dl, $k = 0.139$, for $[\eta] = 0.0$ to 10.9^a

$[\eta]$	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
0.0	1.000	1.010	1.020	1.030	1.041	1.051	1.061	1.072	1.082	1.093
1.0	1.103	1.114	1.125	1.136	1.146	1.157	1.168	1.180	1.191	1.202
2.0	1.213	1.225	1.236	1.248	1.259	1.271	1.283	1.294	1.306	1.318
3.0	1.330	1.342	1.355	1.367	1.379	1.392	1.404	1.417	1.429	1.442
4.0	1.455	1.468	1.480	1.494	1.507	1.520	1.533	1.546	1.560	1.573
5.0	1.587	1.600	1.614	1.628	1.642	1.656	1.670	1.684	1.698	1.713
6.0	1.727	1.742	1.756	1.771	1.786	1.800	1.815	1.830	1.845	1.861
7.0	1.876	1.891	1.907	1.922	1.938	1.954	1.969	1.985	2.001	2.017
8.0	2.034	2.050	2.066	2.083	2.099	2.116	2.133	2.149	2.166	2.183
9.0	2.201	2.218	2.235	2.253	2.270	2.288	2.305	2.323	2.341	2.359
10.0	2.377	2.396	2.414	2.432	2.451	2.470	2.488	2.507	2.526	2.545

^a Figures in columns are η_{rel} values.

TABLE VI
Relationship Between η_{rel} and $[\eta]$ for $c = 0.100$ g/dl, $k = 0.139$, for $[\eta] = 10.0$ to 119

$[\eta]$	0.0	1.0	2.0	3.0	4.0	5.0	6.0	7.0	8.0	9.0
10.0	2.377	2.564	2.762	2.971	3.192	3.425	3.670	3.929	4.203	4.491
20.0	4.794	5.113	5.449	5.803	6.174	6.565	6.976	7.408	7.861	8.338
30.0	8.838	9.362	9.913	10.491	11.096	11.731	12.397	13.095	13.826	14.591
40.0	15.393	16.233	17.112	18.032	18.995	20.003	21.057	22.159	23.312	24.518
50.0	25.779	27.096	28.474	29.913	31.416	32.987	34.628	36.342	38.132	40.001
60.0	41.952	43.989	46.115	48.334	50.649	53.065	55.586	58.215	60.958	63.819
70.0	66.802	69.913	73.157	76.539	80.065	83.740	87.570	91.563	95.723	100.060
80.0	104.570	109.280	114.180	119.290	124.610	130.150	135.920	141.930	148.180	154.700
90.0	161.480	168.540	175.890	183.550	191.510	199.800	208.430	217.410	226.750	236.470
100.0	246.590	257.110	268.060	279.450	291.300	303.620	316.440	329.780	343.640	358.060
110.0	373.060	388.660	404.870	421.730	439.260	457.490	476.430	496.130	516.610	537.890

TABLE VII
Relationship Between η_{rel} and $[\eta]$ for $c = 0.050$ g./dl, $k = 0.139$, for $[\eta] = 0$ to 109

$[\eta]$	0	1	2	3	4	5	6	7	8	9
0	1.0000	1.0508	1.1033	1.1574	1.2132	1.2708	1.3302	1.3915	1.4546	1.5197
10	1.5868	1.6559	1.7270	1.8003	1.8758	1.9535	2.0334	2.1158	2.2004	2.2876
20	2.3772	2.4694	2.5642	2.6617	2.7619	2.8649	2.9708	3.0796	3.1914	3.3063
30	3.4243	3.5456	3.6701	3.7979	3.9292	4.0640	4.2024	4.3444	4.4902	4.6399
40	4.7934	4.9510	5.1126	5.2785	5.4486	5.6231	5.8021	5.9856	6.1738	6.3668
50	6.5647	6.7675	6.9755	7.1886	7.4071	7.6311	7.8605	8.0957	8.3367	8.5835
60	8.8365	9.0956	9.3610	9.6330	9.9115	10.1970	10.4890	10.7880	11.0940	11.4080
70	11.7290	12.0580	12.3950	12.7390	13.0920	13.4530	13.8230	14.2010	14.5880	14.9850
80	15.3900	15.8050	16.2290	16.6640	17.1080	17.5630	18.0280	18.5040	18.9910	19.4890
90	19.9980	20.5190	21.0520	21.5970	22.1540	22.7240	23.3070	23.9030	24.5120	25.1350
100	25.7720	26.4240	27.0900	27.7710	28.4670	29.1780	29.9050	30.6490	31.4080	32.1850

TABLE VIII
Relationship Between η_{rel} and $[\eta]$ for $c = 0.500$ g./dl, $k = 0.139$, for $[\eta] = 0$ to 10.9

$[\eta]$	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
0	1.000	1.051	1.103	1.157	1.213	1.271	1.330	1.392	1.455	1.520
1	1.587	1.656	1.727	1.800	1.876	1.954	2.034	2.116	2.201	2.288
2	2.377	2.470	2.564	2.662	2.762	2.865	2.971	3.080	3.192	3.307
3	3.425	3.546	3.670	3.798	3.929	4.064	4.203	4.345	4.491	4.640
4	4.794	4.951	5.113	5.279	5.449	5.624	5.803	5.986	6.174	6.367
5	6.565	6.768	6.976	7.189	7.408	7.632	7.861	8.097	8.338	8.584
6	8.837	9.097	9.362	9.634	9.913	10.198	10.491	10.790	11.096	11.410
7	11.731	12.060	12.397	12.742	13.094	13.456	13.825	14.204	14.591	14.987
8	15.393	15.808	16.232	16.667	17.112	17.566	18.032	18.508	18.995	19.493
9	20.002	20.524	21.057	21.602	22.159	22.729	23.312	23.909	24.518	25.142
10	25.779	26.430	27.097	27.778	28.474	29.186	29.913	30.657	31.417	32.194

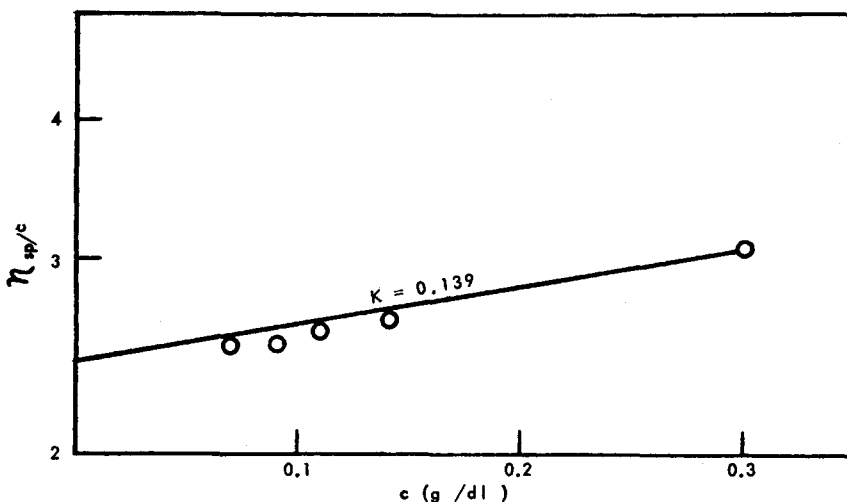


Fig. 3. Martin plot for polyethylene, Sample F: $[\eta]$ by least squares, 2.33; $[\eta]$ from highest point using $k = 0.139, 2.43$, as shown.

to give the desired polymer concentration (generally 0.1 g/dl) is calculated. 0.90 times this volume of Decalin at 25°C is added to the volumetric flask and the sample dissolved by heating, in the usual manner. The flow times of the solvent and of the solution in a suitable viscometer are determined, appropriate kinetic energy corrections being applied. The ratio of these corrected flow times is the relative viscosity, inasmuch as the density of the solution, at these low concentrations, may be considered to be the same as that of the solvent. The value of $[\eta]$ is then read using linear interpolation from the appropriate table (Tables V to VIII) for the concentration used.

These tables are based on Martin's equation, with $k = 0.139$, which may be put in the form

$$\eta_{rel} = 1 + c[\eta]e^{0.320[\eta]c}. \quad (3)$$

While the most generally useful concentration is 0.1 g/dl, tables are included for 0.5 g/dl and 0.05 g/dl. These concentrations should be used for samples having very low and very high $[\eta]$ values, respectively.

DISCUSSION

The conclusion that the Martin equation, eq. (2), fits the experimental data better than the Huggins equation, eq. (1), particularly with the higher $[\eta]$ samples, is in agreement with our experience. Over many years, we have found that the Martin equation has very satisfactorily fitted dilute solution viscosity data for a wide range of polymer-solvent systems. It is somewhat surprising that it is not more generally used. This is probably due in part to the fact that the Huggins equation is somewhat easier to manipulate mathematically.

It is in order to examine various equations for $[\eta]$, especially that of Solomon and Ciuta,³ by which $[\eta]$ may be determined from a single viscosity measurement without the necessity of establishing the value of a slope constant.

Solomon and Ciuta's equation

$$[\eta]c = (2\eta_{sp} - 2 \ln \eta_{rel})^{1/2} \quad (4)$$

may be derived readily by combining Huggins's equation

$$\eta_{sp}/c = [\eta] + k' [\eta]^2 c \quad (1)$$

and Kraemer's equation¹⁶

$$\ln \eta_{rel}/c = [\eta] - k'' [\eta]^2 c \quad (5)$$

remembering that in the limit as c goes to zero, $k' + k'' = 1/2$.

An equivalent derivation of eq. (4) consists of expanding $\ln \eta_{rel}$ and combining this with the Huggins equation, dropping terms in the expansion containing higher powers of $[\eta]$ than $[\eta]^2$.¹⁷

Inasmuch as eq. (4) is a consequence of combining the Huggins and Kraemer equations, it is instructive to consider the implications. Both equations are limiting expressions which are only strictly followed as the concentration approaches zero. Maron and Reznik¹⁸ have pointed out that use of these two equations with experimental data often does not give a common intrinsic viscosity intercept and that the sum of k' and k'' is often not $1/2$. By including higher terms in $[\eta]$ in both eqs. (1) and (5), they have developed a method of plotting dilute solution viscosity data which yields unambiguous values of $[\eta]$ and maintains the equality $k' + k'' = 1/2$. Their treatment, however, does not readily lend itself to use in a one-point $[\eta]$ method.

In light of these considerations, it is apparent that equations derived by algebraic manipulations of equivalent limiting expressions are essentially "bootstrap operations" and that, if one expression really describes the viscosity-concentration behavior, the other cannot, unless higher terms of the two expansions are included. Thus, if Solomon and Ciuta's equation yields the correct value of $[\eta]$, it is due to a balancing of the approximations involved in discarding terms involving $[\eta]$ to higher powers than the second. Gillespie and Hulme¹⁹ have carried out an analysis of the Solomon and Ciuta equation and find that it should give results in agreement with the Huggins equation when k' in the latter is $1/3$.

Tables V to VIII based upon Martin's equation and the experimental value of the slope constant ($k = 0.139$) provide a means of testing whether or not Solomon and Ciuta's equation gives the correct value of $[\eta]$. It is found that the $[\eta]$ values calculated from η_{rel} in the tables, using their equation, are in good agreement with those in the tables up to $[\eta]c = 1$. Above this point, the deviation rapidly becomes serious. This confirms the analysis of Gillespie and Hulme, inasmuch as in the limit, as the concentration approaches zero, Huggins's slope constant k' is equal to $2.303k$, Martin's

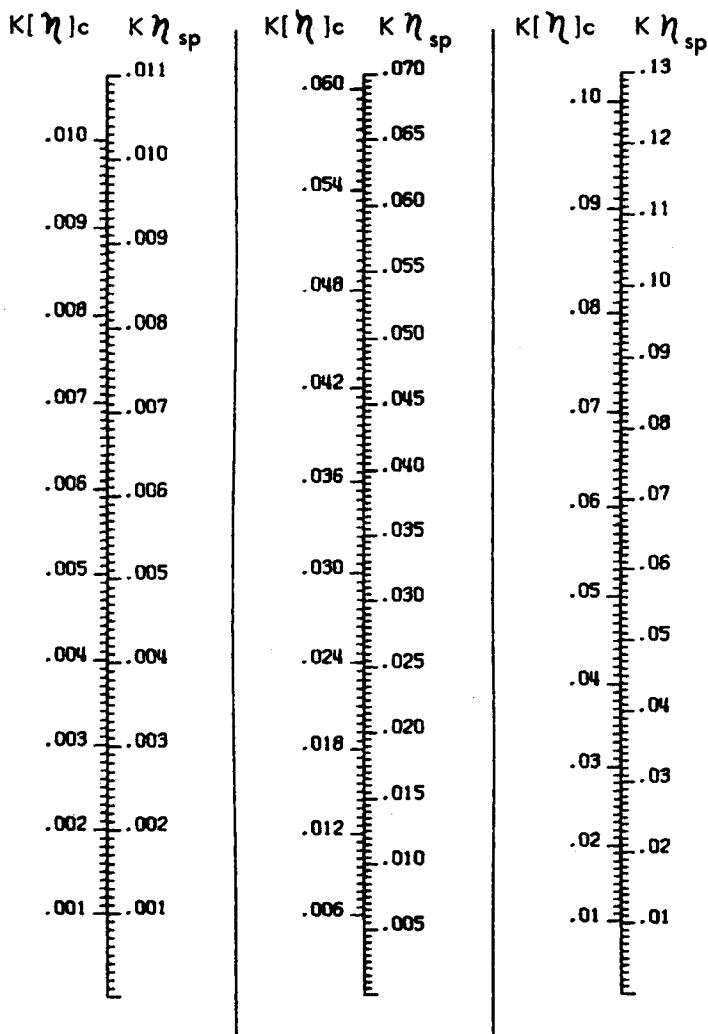


Fig. 4. Relationship between $k[\eta]c$ and $k\eta_{sp}$

slope constant.¹⁴ This yields a limiting value of k' of 0.32 in agreement with their analysis.

Spurlin has pointed out to us that the Martin equation may be put into the form

$$\log(k\eta_{sp}) = \log(k[\eta]c) + k[\eta]c. \quad (6)$$

The right-hand side of this equation is of the form $\log X + X$ where X is $k[\eta]c$. This permits universal graphs to be constructed of $k[\eta]c$ versus $k\eta_{sp}$. Now if k is established experimentally and η_{sp} determined at a known concentration, $[\eta]$ may be determined from the graphs by simple arithmetic

operations. A set of graphs based upon eq. (6) and covering the three decades of $k[\eta]c$ encountered in practical $[\eta]$ determinations is given in Figures 4 and 5. It should be emphasized that such graphs are applicable to any polymer-solvent system which is described by the Martin equation and for which the value of k is known. It is hoped that these graphs may lead to the more general use of the Martin equation.

These graphs can be read to approximately 1%. It must be remembered, however, that routine viscosity measurements are seldom this accurate. In the exceptional case where more precision is really needed, it is easily obtained by linear interpolation, i.e., back calculating η_{sp} from the Martin equation for two close values of $[\eta]$.

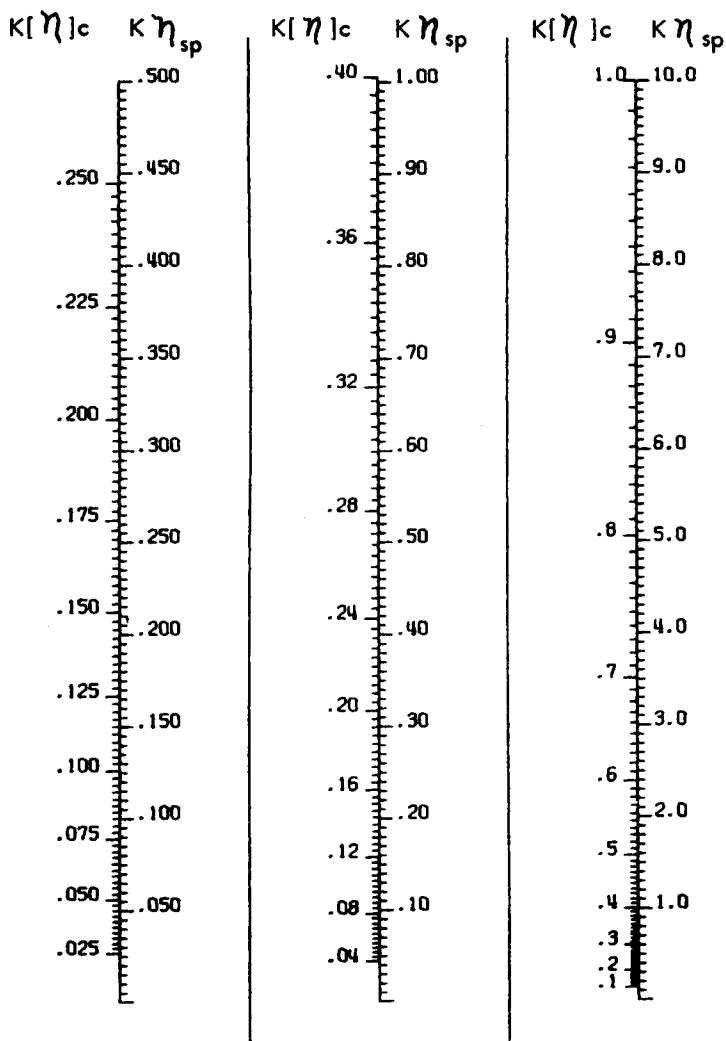


Fig. 5. Relationship between $k[\eta]c$ and $k\eta_{sp}$.

CONCLUSIONS

An analysis of an extensive series of experimental dilute solution viscosity data covering a wide range of polyethylene and polypropylene samples in Decalin at 135°C has shown that the data are fitted better by the Martin than by the Huggins equation. It was found that a grand average slope constant ($k = 0.139$) in the Martin equation was applicable to both of these polymers. Based on this, a series of tables have been prepared which permit the calculation of the intrinsic viscosity from a single relative viscosity measurement, at an appropriate fixed concentration. Use of this one-point method with the experimentally established average slope constant should, in general, give more accurate values for $[\eta]$ than the conventional multipoint method.

It was found that the equation of Solomon and Ciuta also yields acceptable $[\eta]$ values for these particular polymer-solvent systems. This is a consequence of the experimental value of the Martin slope constant which leads to a limiting Huggins k' of 0.32, which happens to be close to the value of $k' = 0.33$ inherent in the Solomon and Ciuta equation.

The Martin equation has been put into a "universal form" which permits its use for obtaining $[\eta]$ from a single specific viscosity measurement for any value of the Martin slope constant and concentration. It is hoped that this relationship and the graphs based upon it may encourage the wider use of the Martin equation, which we have found to be the most generally applicable relationship for intrinsic viscosity determinations for a very wide variety of polymer-solvent systems. We shall be happy to send a full-sized set of these graphs to interested readers.

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