A New Equation for Estimating [η] from Single-Viscosity Measurement in Dilute Solution*

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SYNOPSIS

The use of a linear two-parameter approximation for determining limiting viscosity number, [η], of a polymer in the state of infinite dilution requires considerable amount of time, effort, and materials. Several workers who attempted to estimate [η] directly from single-viscosity measurement also proposed equations for this purpose. Such equations are tested and found to have good applicability to practical data within specified limits of concentration or specific viscosity. A new equation has been derived and tested for polymers of high and low molecular weights in various solvents and at different temperatures. The introduction of a constant in this equation makes it applicable over a wider range of specific viscosity. It is found to serve better for determination of [η] from a single-viscosity measurement.

INTRODUCTION

Limiting viscosity number, [η], which characterizes the polymer in the state of infinite dilution is probably the most frequently measured property for estimating the interaction and solution parameters. The following mathematical equations often used for determining [η] are found to hold good at low concentration (less than 2%) of polymer in solution.

$$[\eta] = \frac{\eta_{sp}}{C} - K_H[\eta]^2 C \quad \text{(Huggins}^1) \tag{1}$$

$$= \frac{1}{K_M C} - \left(\log\left(\frac{\eta_{sp}}{C}\right) - \log[\eta] \right) \quad \text{(Martin}^2) \tag{2}$$

$$= \frac{\ln \eta_r}{C} + K_K[\eta]^2 C \quad \text{(Kreamer}^3) \tag{3}$$

$$= \frac{\eta_{sp}}{C} - K_S[\eta]\eta_{sp} \quad \text{(Schulz–Blaschke}^4) \tag{4}$$

Maron and Reznik[5] derived the following equation by using the expanded forms of Huggins and Kraemer's equations.

$$\frac{\eta_{sp} - \ln \eta_r}{C^2} = \frac{[\eta]^2}{2} + (k_1 - \tfrac{1}{3})[\eta]^3 C \tag{5}$$

where k_1 is the Huggins constant. Maron and Reznik tested the applicability of this equation to dilute polymer solution as well as to the solutions of polymer blends. They are of the opinion that their equation provides a linear means of plotting viscosity data for dilute polymer solutions by yielding unambiguous intrinsic viscosity and satisfies the objections that have been raised against other methods.

In using any one of the above equations, a considerable amount of time, effort, and materials are lost in conducting experiments at series of concentrations and then implying a linear two-parameter approximation to the data. This led several workers to estimate the limiting viscosity directly from a single measurement of specific viscosity and attempt to propose an equation for obtaining [η] and discuss[6–8] the limitations. A few of such equations are given below with abbreviations of authors cited given in brackets for ease of discussion.

$$[\eta] = \frac{\sqrt{2}}{C} \{ \eta_{sp} - \ln \eta_r \}^{1/2}$$

$$\text{[Solomon and Ciuta}^9 \text{ (SC)]} \tag{6}$$

$$= \frac{\eta_{sp}}{C} \frac{1 + 0.28\eta_{sp}}{1 + (K_H + 0.28)\eta_{sp}}$$

$$\text{[Khan and Bhargava}^{10} \text{ (KB)]} \tag{7}$$

$$= \frac{1}{C} \{ 3 \ln \eta_r + (\tfrac{3}{2})\eta_{sp}^2 - 3 \eta_{sp} \}^{1/3}$$

[Deb and Chatterjee[11] (DC)] (8)

$$= \frac{\eta_{sp}}{C} (1 + 0.24 \eta_{sp}^{-1})$$

[Rudin and Wagner[12] (RW)] (9)

$$= \frac{1}{2C} (\eta_{sp} + \ln \eta_r)$$

[Ram Mohan Rao and Yaseen[13] (RY)] (10)

Chee[14] compared the general validity of the above equations for determining [η] and suggested that the Huggins, SC, DC, and RY equations could be expanded in the following form:

$$[\eta]C = \eta_{sp} (1 - K_H \eta_{sp} + 2K_H^2 \eta_{sp}^2 ...) \quad \text{Huggins} \quad (11)$$

$$= \eta_{sp} [1 - (\tfrac{1}{3})\eta_{sp} + (\tfrac{7}{36})\eta_{sp}^2 ...] \quad \text{SC} \quad (12)$$

$$= \eta_{sp} [1 - (\tfrac{1}{4})\eta_{sp} + (\tfrac{11}{80})\eta_{sp}^2 ...] \quad \text{DC} \quad (13)$$

$$= \eta_{sp} [1 - (\tfrac{1}{4})\eta_{sp} + (\tfrac{1}{6})\eta_{sp}^2 ...] \quad \text{RY} \quad (14)$$

All of these equations hold good for values of η_{sp} < 1.0.

Chee is of the opinion that Eqs. (12)–(14) are special cases of Eq. (11) with the coefficient K_H being equal to 0.33, 0.25, and 0.25, respectively. He also proposed the following equation for the routine and quick calculation of [η] in the laboratory with good degree of reliability.

$$[\eta] = \frac{\eta_{sp} - aC^2}{C(1 + bC)} \quad (15)$$

Here a and b are constants that have to be predetermined before obtaining [η] values.

Balke[15] examined critically the above expanded series forms using a computer-generated form as the basis for the assessment and suggested that Eqs. (11)–(14) could be expressed in the following form:

$$[\eta] = \left\{ \frac{\eta_{sp}}{C} \right\} Z \quad (16)$$

Here Z is defined as a correction factor, the value of which transforms the specific viscosity–concentration ratio measured at a finite concentration, to a value at infinite dilution.

The applicability of most of the single-point equations is limited to a certain concentration or specific viscosity. Solomon and Ciuta recommended an operating concentration of about 0.2%, whereas Deb and Chatterjee used their equation upto 2.5% concentration of the polymer. Ram Mohan Rao and Yaseen pointed out that for getting good results from

single-point equations, concentration should not be the sole criterion as η_{sp}; the main component of the single-point equation depends on the molecular weight of the polymer. They observed satisfactory results by using single-point equations when η_{sp} is less than 0.2.

The main variable of single-point equations is concentration, consequently the η_{sp}. Their applicability is found to be good when relatively low value of η_{sp} is used. The aim of the present study is to derive an equation that could be applicable to a wider range of η_{sp} values.

A NEW EQUATION FOR ESTIMATING [η] FROM A SINGLE η_{sp} VALUE

An equation has been derived by equating Martin's equation [Eq. (2)] to Schulz–Blaschke's equation [Eq. (4)]:

$$\frac{1}{K_M C} \left(\log \left(\frac{\eta_{sp}}{C} \right) - \log [\eta] \right) = \frac{\eta_{sp}}{C} - K_S [\eta] \eta_{sp} \quad (17)$$

$$\log [\eta] = \log \left(\frac{\eta_{sp}}{C} \right) - K_M \eta_{sp} + K_M K_S C [\eta] \eta_{sp} \quad (18)$$

In a dilute solution the contribution of the product of multiple of factors K_M, K_S, C, [η], and η_{sp} whose individual value is <1.0 becomes negligible. Consequently, Eq. (18) can be expressed in the following form with constant K_M being equivalent to K.

$$\log [\eta] = \log \left(\frac{\eta_{sp}}{C} \right) - K \eta_{sp} \quad (19)$$

This equation is found to have better fit with practical data when K = 0.14 for η_{sp} < 0.3 and K = 0.12 for η_{sp} > 0.3 and < 0.8. The validity of the proposed equation has been tested using reported data as well as practical data generated in the laboratory.

EXPERIMENTAL

Commercial-grade nylon 6 (M/s Gujarat State Fertilizers Company Limited, Baroda, India) having viscosity average molecular weight of 35,000 was used for conducting viscosity measurements at different temperatures (Schott Geräte thermostatic control) using Ubbelohde capillary viscometer and AVS/N system for automatic recording of flow time to the accuracy of 0.01 of a second.[16,17]

RESULTS AND DISCUSSION

The applicability of the proposed equation was assessed by using reported viscosity data as well as practical data. Specific viscosity and concentration data reported in Rudin and Wagner[12] were used in calculating $[\eta]$ values by using SC, KB, DC, and RY equations and the proposed equation. These values along with extrapolated values of $[\eta]_E$ from two different methods are reported in Table I for comparison. The results indicate that the values of $[\eta]$ obtained from SC and KB equations and from the proposed equation are having very good agreement with $[\eta]_E$ values, whereas the values of $[\eta]$ from RY and DC equations are a little higher. But in cases where η_{sp} less than 0.2 was used, the values of $[\eta]$, calculated by using any one of these single-point equations, are in good agreement with $[\eta]_E$.

It seems that Nero and Sikdar[8] used sets of data for the solutions of various fractions of a polymer in particular solvent, accordingly the same are grouped in Table II. They tested the applicability of various single-point equations and drew the conclusion that the SC equation produced better results in comparison to other equations. The practical data of Nero and Sikdar have been used for testing the applicability of the proposed equation and compared the results with those obtained from other single-point equations. The calculated values of $[\eta]$ along with η_{sp}, concentration and $[\eta]_E$ from two different methods are reported in Table II. The results show that when η_{sp} is fairly high, the calculated values of $[\eta]$ obtained from different equations do not find so close a fit with $[\eta]_E$. However, at most concentrations, the values of $[\eta]$ obtained from proposed equation are in fairly good agreement with the value

of $[\eta]_E$. The values of $[\eta]$ obtained from the proposed equation are found to be in better agreement with $[\eta]_E$ of Maron and Reznik.

Ram Mohan Rao and Yaseen[16] used 10 different solvents for determining η_{sp} at various concentrations of alkyd resin using a sophisticated automatic setup of recording the flow time. The results reported in Table III show good applicability of single-point equations to their practical data. They are of the opinion that for better applicability of single-point equations, η_{sp} should be taken as a criterion, not the concentration of the polymer in solution.[13]

Results reported in Tables I to III are related to viscosity measurements conducted at a specific temperature. In view of testing the applicability of the proposed equation, viscosity data of nylon 6 in m-cresol determined at temperatures ranging from 20 to 75°C are considered for discussion. The critical analysis of data in Table IV shows that $[\eta]$ values obtained from SC, KB, and proposed equations are having very good agreement with values of $[\eta]_E$ at all temperatures, whereas the values of $[\eta]_{RY}$ and $[\eta]_{DC}$ are at a little higher side.

ASSESSMENT OF THE PROPOSED EQUATION

$$\log [\eta] = \log \left(\frac{\eta_{sp}}{C}\right) - K\eta_{sp}$$

The introduction of a constant, K, in the preceding equation makes its applicability more flexible. The value of K may be varied from 0.1 to 0.15 to cover a wide range of practical viscosity data. In our

Table I   Comparison of [n] Values[a] Obtained from Different Equations by Using Data Reported by Rudin and Wagner[12]

| System | | | | | | | | Extrapolated $[\eta]_E$ from | |
Polystyrene M_w/Solvent	Conc. g/dL	n_{sp}	$[n]_{SC}$	$[n]_{KB}$	$[n]_{RY}$	$[n]_{DC}$	$[n]_P$	Eq. 5	Eq. 1
1.46×10^6 (toluene)	0.090	0.250	2.570	2.580	2.630	2.630	2.560	—	2.600
1.06×10^6 (toluene)	0.250	0.560	1.920	1.930	2.010	2.000	1.920	2.114	1.930
	0.325	0.730	1.850	1.870	1.970	1.950	1.840		
0.5×10^6 (toluene)	0.125	0.150	1.140	1.140	1.160	1.540	1.140	1.183	1.150
	0.240	0.290	1.110	1.110	1.130	1.130	1.110		
1.46×10^6 (2-butanone : isopropanol 6 : 1 by vol.)	0.100	0.080	0.780	0.780	0.785	0.785	0.780	0.760	0.790
	0.180	0.150	0.795	0.795	0.805	0.804	0.794		
0.5×10^6	0.240	0.130	0.519	0.520	0.525	0.525	0.519	—	0.520

[a] The unit of [n] is dL/g; $[\eta]_P$ from Eq. 19.

Table II   Comparison of [n] Values[a] Obtained from Different Equations by Using Data Reported by Nero and Sikdar[8]

System	Conc. g/dL	n_{sp}	$[n]_{SC}$	$[n]_{KB}$	$[n]_{RY}$	$[n]_{DC}$	$[n]_P$	Extrapolated $[\eta]_E$ from Eq. 5	Eq. 1
Polyester–imide in chloroform	1.026	0.627	0.516	0.520	0.543	0.539	0.513	0.512	0.518
	0.342	0.186	0.513	0.514	0.521	0.519	0.512		
	0.853	0.305	0.327	0.328	0.355	0.334	0.329	—	0.325
	0.975	0.471	0.423	0.425	0.439	0.438	0.424	0.424	0.431
	0.325	0.144	0.423	0.424	0.428	0.428	0.423		
	0.117	0.033	0.279	0.279	0.280	0.279	0.279	0.278	0.284
	0.586	0.175	0.282	0.283	0.287	0.287	0.287		
Polyphenyline oxide in chloroform	1.329	0.656	0.414	0.417	0.436	0.433	0.411	—	0.429
	0.714	0.209	0.275	0.275	0.279	0.279	0.276	0.273	0.280
	0.416	0.118	0.274	0.274	0.276	0.275	0.274		
	1.757	0.723	0.341	0.344	0.361	0.357	0.337	0.341	0.344
	0.586	0.213	0.341	0.341	0.341	0.347	0.340		
Polycarbonate in chloroform	0.987	0.574	0.497	0.500	0.521	0.518	0.500	0.484	0.493
	0.329	0.168	0.484	0.485	0.492	0.490	0.484		
	1.023	0.795	0.633	0.640	0.674	0.677	0.624	0.639	0.638
	0.512	0.362	0.627	0.629	0.645	0.644	0.631		
	0.956	0.362	0.341	0.342	0.343	0.346	0.343	0.342	0.341
	0.319	0.113	0.342	0.343	0.346	0.343	0.342		
	1.099	0.283	0.236	0.237	0.242	0.241	0.235	0.236	0.239
	0.366	0.089	0.235	0.236	0.238	0.230	0.236		

[a] The unit of [n] is dL/g; $[\eta]_P$ from Eq. 19.

Table III   Comparison of [n] Values[a] Obtained from Different Equations by Using Data Reported by Ram Mohan Rao and Yaseen[13] for Linseed Oil Alkyd

Solvent	Conc. g/dL	n_{sp}	$[n]_{SC}$	$[n]_{KB}$	$[n]_{RY}$	$[n]_{DC}$	$[n]_P$	Extrapolated $[\eta]_E$ from Eq. 5	Eq. 1
Benzene	0.550	0.057	0.101	0.101	0.101	0.102	0.101	0.102	0.101
	0.908	0.094	0.101	0.101	0.102	0.102	0.101	—	—
Toluene	0.273	0.027	0.096	0.096	0.097	0.097	0.096	0.096	0.096
	1.994	0.208	0.098	0.098	0.099	0.099	0.097	—	—
Ethyl acetate	0.501	0.049	0.095	0.095	0.096	0.096	0.095	0.096	0.096
	2.071	0.210	0.095	0.095	0.096	0.096	0.095	—	—
Ethyl benzene	0.408	0.038	0.092	0.092	0.093	0.093	0.092	0.092	0.092
	1.250	0.120	0.092	0.093	0.093	0.093	0.092	—	—
MEK	0.326	0.030	0.091	0.091	0.091	0.091	0.091	0.091	0.091
	1.015	0.095	0.091	0.091	0.092	0.092	0.091	—	—
Acetone	0.414	0.029	0.068	0.068	0.069	0.069	0.068	0.067	0.067
	1.305	0.095	0.071	0.071	0.071	0.071	0.071	—	—
THF	0.264	0.019	0.071	0.071	0.072	0.072	0.071	0.071	0.070
	0.643	0.048	0.073	0.073	0.073	0.073	0.073	—	—
Cyclohexane	0.367	0.021	0.058	0.058	0.058	0.058	0.058	0.057	0.057
	1.076	0.060	0.060	0.060	0.060	0.060	0.060	—	—
Cyclohexanone	0.789	0.047	0.058	0.058	0.058	0.058	0.058	0.056	0.056
	2.209	0.147	0.063	0.063	0.064	0.064	0.063	—	—

[a] The unit of [n] is dL/g; $[\eta]_P$ from Eq. 19.

Table IV Comparison of [n] Values[a] of Nylon 6 in *m*-cresol at Different Temperatures

Temperature (°C)	Conc. g/dL	n_{sp}	[n]$_{SC}$	[n]$_{KB}$	[n]$_{RY}$	[n]$_{DC}$	[n]$_{P}$	Extrapolated $[\eta]_E$ from Eq. 5	Extrapolated $[\eta]_E$ from Eq. 1
20	0.1243	0.2305	1.728	1.731	1.762	1.759	1.726	1.728	1.729
25	0.1238	0.2195	1.658	1.658	1.689	1.686	1.652	1.658	1.658
30	0.1234	0.2142	1.625	1.627	1.654	1.653	1.620	1.627	1.628
35	0.1229	0.2105	1.606	1.607	1.634	1.632	1.600	1.603	1.605
40	0.1224	0.2051	1.573	1.575	1.600	1.598	1.569	1.574	1.575
45	0.1219	0.2032	1.566	1.568	1.592	1.591	1.561	1.564	1.566
50	0.1214	0.1950	1.512	1.514	1.536	1.535	1.508	1.575	1.518
55	0.1209	0.1910	1.489	1.490	1.513	1.511	1.486	1.490	1.492
60	0.1205	0.1880	1.472	1.473	1.495	1.494	1.468	1.475	1.478
65	0.1200	0.1840	1.448	1.450	1.470	1.469	1.445	1.445	1.443
70	0.1194	0.1810	1.433	1.434	1.455	1.453	1.430	1.434	1.432

[a] The unit of [n] is dL/g; $[\eta]_P$ from Eq. 19.

calculations two values of K have been used for estimating $[\eta]$ values reported in this study, i.e., $K = 0.14$, when η_{sp} values are < 0.3 and $K = 0.12$, when $\eta_{sp} > 0.3$ and < 0.8. The proposed equation has been tested for a variety of polymers of high and low molecular weights in various solvents and at different temperatures. It is found to have good applicability to a wider range of η_{sp} values. The proposed equation is found to serve better for determining $[\eta]$ from single measurement of viscosity and in its applicability η_{sp} is taken as the criterion.

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