

Determination of Intrinsic Viscosity by Single Specific Viscosity Measurement

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Synopsis

Single point determination of intrinsic viscosity saves considerable amount of time, effort and materials. Quite a few equations are available in the literature which require relative viscosity of the polymer solution at a single concentration for calculation of $[\eta]$. A comparative assessment of the applicability of two such equations and that of a proposed one has been made by using reported data as well as the practical data on viscosity of alkyd solutions in different solvents. It is inferred from the findings that, for good results from single point methods, the concentration should not be the sole criterion, as suggested by earlier workers; η_{sp} may also be considered as one of the criteria. The single point technique is found to be applicable to alkyd solutions in different solvents.

INTRODUCTION

A fairly good number of mathematical equations are available for determining the intrinsic viscosity $[\eta]$ of a polymer solution. The following most commonly used equations require practical data for specific viscosity η_{sp} or relative viscosity η at a few concentrations C of the polymer in a solvent:

$$[\eta] = \eta_{sp}/C - K_1[\eta]^2C \text{ Huggins}^1 \quad (1)$$

$$[\eta] = \eta_{sp}/C - K_2[\eta]\eta_{sp} \text{ Schulz and Blaschke}^2 \quad (2)$$

$$[\eta] = \ln \eta/C + K_3[\eta]^2C \text{ Kraemer}^3 \quad (3)$$

These are found to hold good at low concentrations, and the graphical extrapolation of any one of them is expected to produce more or less the same value of $[\eta]$ of the polymer in a solvent. In doing so a considerable amount of time, efforts, and materials are lost in conducting experiments at series of concentrations and then implying a linear two-parameter approximation to the data. Sometimes, the graphical solutions do not provide so accurate estimation of $[\eta]$. Elliot et al.^{4,5} found that the $[\eta]$ determined by the conventional multipoint method was not so accurate compared to that calculated by using single relative viscosity and an average value of K (slope constant) for a given polymer-solvent system. Taking these aspects into consideration, some workers⁶⁻¹⁰ have proposed equations which require the viscosity of the polymer at a single concentration in a solvent of known viscosity for calculating $[\eta]$.

These equations are useful in calculating intrinsic viscosity with permissible degree of accuracy when the concentration of the polymer in so-

lution and the choice of solvents are within the prior validation limits.⁶ Solomon and Ciuta⁷ verified their proposed equation for different polymer-solvent systems and recommended an operating concentration of about 0.2% for the calculated $[\eta]$ values to accord with those obtained from extrapolation. Catsiff¹¹ pointed out the need of experimental determination of Huggins constant K_1 and the other related parameter while commenting on the applicability of Solomon and Ciuta's equation as single point method. Nero and Sikdar¹² preferred Solomon and Ciuta's equation in comparison to other methods as they felt it had a means of testing the correctness of the single point $[\eta]$ value. Deb and Chatterjee⁸ found that $[\eta]$ values calculated by using the equation proposed by them are in good agreement with those obtained from the Schulz and Blaschke's equation. Rudin and Wagner⁶ are of the opinion that single point techniques are more reliable for low concentration data particularly in the case of polymer-solvent systems having Huggins constant K_1 around 1/3. They suggested a model which takes into account the existence of noninterpenetrating solvated spherical entities upto a certain critical concentration.⁶

In an exercise of analyzing the practical and reported viscosity data considerable variations were observed in the values of $[\eta]$ calculated by using the reported equations.^{7,8} Because of this an equation based on a simple assumption is proposed so that the calculated $[\eta]$ may fit better with that from extrapolation.

THE PROPOSED EQUATION

Consider the variables in eqs. (1) and (3); η_{sp} is always greater than $\ln \eta$. However, at a very low concentration, $\eta_{sp} - \ln \eta$ becomes negligible and factors $K_1[\eta]^2C$ and $K_3[\eta]^2C$ are not likely to make significant contribution to $[\eta]$. At low concentration of the polymer in a solution, the difference between the values of η_{sp} and $\ln \eta$ and that between the values of $K_1[\eta]^2C$ and $K_3[\eta]^2C$ may be within such limits that an average of η_{sp}/c and $\ln \eta/c$ can be equated to $[\eta]$. Taking these aspects into consideration, the following equation is suggested for calculating $[\eta]$ within tolerable limits:

$$[\eta] = (1/2C)(\eta_{sp} + \ln \eta) \quad (4)$$

This equation is simple and may find good applicability to a variety of polymer-solvent systems when the single relative viscosity measurement is made at a low concentration.

The validity of this equation has been tested by using experimentally determined and reported data and the results are compared with those obtained from the following equations:

$$[\eta] = (1/C)\sqrt{2(\eta_{sp} - \ln \eta)} \quad \text{Solomon and Ciuta}^7 \quad (5)$$

$$[\eta] = (1/C) \left[3 \ln \eta + \frac{3}{2} \eta_{sp}^2 - 3\eta_{sp} \right]^{1/3} \quad \text{Deb and Chatterjee}^8 \quad (6)$$

EXPERIMENTAL

Ten Analytical grade solvents, five poorly hydrogen bonded and five moderately hydrogen bonded, were selected on the basis of their solvency power for the two resins, i.e., (i) linseed alkyd, the semipolymerized 66% linseed oil-pentaerythritolphthalate, and (ii) DCO-alkyd, the semipolymerized 73% dehydrated castor oil-pentaerythritolphthalate.^{13,14} In each solvent the viscosity of alkyd solutions (at least six concentrations, i.e., approx. 0.5–2.5%) was determined at $25 \pm 0.004^\circ\text{C}$ (Schott-Geräte thermostatic control) using Ubbelohde capillary viscometer and AVS/N system for automatic recoding of flow time to an accuracy of 0.01 of a second. The viscosity data of the resin were treated by using Huggins' equation for determining its intrinsic viscosity in a solvent by extrapolation.

RESULTS

A comparative assessment of the applicability of eqs. (4)–(6) in calculating $[\eta]$ from single concentration viscosity measurement has been made by using data reported by Rudin and Wagner,⁶ Solomon and Ciuta,⁷ Deb and Chatterjee,⁸ and Nero and Sikdar,¹² and the results are given in Tables I–IV. Practical data have also been used for assessing the applicability of single point methods to alkyd solutions in different types of solvents. The results are reported in Tables V and VI.

DISCUSSION

Solomon and Ciuta derived their equation assuming that the sum of the constants K_1 and K_3 is 0.5. While analysing their data with the help of Huggins' equation, it is found that value of constant K_1 is about 0.35 in the case of systems reported by them. Hence their assumption may be justifiable as K_3 is always less than K_1 . They found that their equation has good applicability even at higher concentrations but recommended an

TABLE I
Comparison of Calculated $[\eta]$ with Its Extrapolated Value^a

System	Concentration (g/dL)	η_{sp}	$[\eta]_D$	$[\eta]_S$	$[\eta]_P$	$[\eta]_E$
Synthetic rubber in toluene	0.200	0.248	1.173	1.150	1.174	1.16
Cis-1,4-polyisoprene rubber	0.228	0.349	1.418	1.380	1.422	1.40
	0.232	0.281	1.140	1.110	1.140	1.10
Cellulose	0.190	0.277	1.370	1.340	1.372	1.32
Polystyrene in toluene	0.200	0.334	1.552	1.510	1.555	1.48
Polystyrene in methyl ethyl-ketone	0.200	0.176	0.844	0.830	0.845	0.82
Polystyrene in <i>p</i> -xylene	0.220	0.128	0.563	0.560	0.565	0.54

^a Data reported in Solomon and Ciuta's paper⁷ are used for the above calculations: $[\eta]_D$ = intrinsic viscosity calculated by using Deb and Chatterjee's equation⁸; $[\eta]_S$ = intrinsic viscosity calculated with Solomon and Ciuta's equation; $[\eta]_P$ = intrinsic viscosity calculated with the proposed equation; and $[\eta]_E$ = intrinsic viscosity obtained from extrapolation.

TABLE II
 Comparison of Calculated $[\eta]$ with Its Extrapolated Value^a

System	Concentration (g/dL)	η_{sp}	$[\eta]_D$	$[\eta]_S$	$[\eta]_P$	$[\eta]_E$
Polystyrene in benzene						
FS-1	0.5	2.137	3.14	2.82	3.28	3.12
FS-2	0.5	1.745	2.65	2.42	2.75	2.70
FS-6	0.5	0.845	1.42	1.36	1.46	1.42
FS-9	0.5	0.420	0.76	0.74	0.77	0.75
FS-10	0.5	0.330	0.61	0.59	0.61	0.61
Polyvinyl acetate in benzene						
F-3	0.5	0.596	1.05	1.01	1.063	1.04
F-8	0.5	0.306	0.57	0.56	0.573	0.57
F-11	0.5	0.187	0.353	0.35	0.358	0.355
Polystyrene in toluene						
F-4	0.6	0.958	1.34	1.26	1.358	1.36
F-10	0.6	0.251	0.39	0.39	0.396	0.39

^a Data reported in Deb and Chatterjee's paper⁸ are used for the above calculations.

operating concentration of about 0.2%. Taking this into consideration, the data for polymer solutions having around 0.2% concentration reported in Solomon and Ciuta's⁷ paper are used for calculating $[\eta]$. The calculated values of $[\eta]$ obtained from Solomon and Ciuta's equation are found to have better agreement with extrapolated $[\eta]$ than those obtained either from Deb and Chatterjee's equation or from the proposed one. The values reported in Columns $[\eta]_D$ and $[\eta]_P$ (Table I) are found to have fairly good agreement with each other; however, compared to those in columns $[\eta]_S$ and $[\eta]_E$, they are a little greater and in no case more than 5%.

Deb and Chatterjee derived their equation by combining Huggins' and Schulz and Blaschke's equations, assuming that higher polynomial terms became negligible at low concentrations and $\eta_{sp} < 1$. The data reported by Deb and Chatterjee are used for testing these equations, and the calculated values of $[\eta]$ are given in columns $[\eta]_D$, $[\eta]_S$, and $[\eta]_P$ in Table II. Deb and Chatterjee have used η_{sp} values even greater than 2 while testing the equations with their practical data. The values of $[\eta]$ obtained from the proposed equation are found to have good agreement with extrapolated $[\eta]$; however, they are not so close as in the case of $[\eta]$ values from Deb and Chatterjee's equation. When the η_{sp} value is low, for example, in the case of polystyrene

 TABLE III
 Intrinsic Viscosity $[\eta]$ Obtained from Solution Properties of Polystyrenes^a

Polymer polystyrene	Concentration (g/dL)	η_{sp}	$[\eta]_D$	$[\eta]_S$	$[\eta]_P$	$[\eta]_E$
$\overline{M}_w = 1.46 \times 10^6$ (toluene)	0.090	0.25	2.63	2.57	2.63	2.60
$\overline{M}_w = 1.08 \times 10^6$ (toluene)	0.325	0.73	1.95	1.85	1.97	1.93
$\overline{M}_w = 0.5 \times 10^6$ (toluene)	0.125	0.15	1.15	1.14	1.16	1.15
$\overline{M}_w = 1.46 \times 10^6$ [6:1 (vol) 2-butanone:isopropanol]	0.100	0.08	0.794	0.780	0.785	0.790
$\overline{M}_w = 0.5 \times 10^6$	0.240	0.13	0.525	0.519	0.525	0.520

^a Data reported in Rudin and Wagner's paper⁶ are used for the above calculations.

TABLE IV
Comparison of Calculated $[\eta]$ with Its Extrapolated Value*

System	Concentration					
	(g/dL)	η_{sp}	$[\eta]_D$	$[\eta]_S$	$[\eta]_P$	$[\eta]_E$
Polyetherimide in chloroform	1.0264	0.6272	0.539	0.516	0.543	0.518
	0.3420	0.1860	0.519	0.513	0.521	0.518
	0.2843	0.0941	0.327	0.321	0.324	0.325
Polyphenylene oxide in chloroform	0.3251	0.1440	0.428	0.423	0.428	0.431
	1.3291	0.6556	0.433	0.414	0.436	0.429
	0.4430	0.1082	0.428	0.421	0.428	0.429
	0.7140	0.2090	0.279	0.275	0.279	0.280
Polycarbonate in chloroform	0.4160	0.1182	0.275	0.274	0.276	0.280
	0.3290	0.1681	0.490	0.484	0.492	0.493
	0.5116	0.3560	0.644	0.627	0.645	0.638
	1.0991	0.2825	0.241	0.236	0.242	0.239
	0.3663	0.0891	0.230	0.235	0.238	0.239

* Data reported in Nero and Sikdar's paper¹² are used for the above calculations.

fraction FS-10 ($\eta_{sp} = 0.330$) the values of $[\eta]$ calculated by using any one of these equations have very good agreement with the extrapolated one. Similar feature is observed in the case of other polymer fractions which have low η_{sp} values (Table II).

The testing of these equations is also done with the data which Rudin and Wagner used in assessing the applicability of their single point equation.⁶ The values of $[\eta]_D$, $[\eta]_S$, and $[\eta]_P$ calculated by using data reported in their paper are found to have good agreement with extrapolated $[\eta]$ at

TABLE V
Comparison of Calculated $[\eta]$ with Extrapolated $[\eta]$ Value of Linseed Oil-Alkyd in Different Solvents*

Solvent	Concentration					
	(g/dL)	η_{sp}	$[\eta]_D$	$[\eta]_S$	$[\eta]_P$	$[\eta]_E$
Benzene $\delta_s = 9.15$	0.5505	0.0567	0.1063	0.1011	0.1016	0.1015
	1.4091	0.1480	0.1012	0.1002	0.1015	
Toluene $\delta_s = 8.91$	0.2727	0.0265	0.0961	0.0963	0.0965	0.0965
	1.9943	0.2081	0.0994	0.0979	0.0995	
Ethyl acetate $\delta_s = 9.1$	0.5014	0.0486	0.0956	0.0954	0.0958	0.0960
	2.0715	0.2096	0.0966	0.0948	0.0965	
Ethyl benzene $\delta_s = 8.8$	0.4080	0.0382	0.0903	0.0925	0.0928	0.0928
	0.8762	0.0826	0.0906	0.0918	0.0924	
Methyl ethyl ketone $\delta_s = 9.27$	0.3259	0.0300	0.0954	0.0911	0.0914	0.0915
	1.0148	0.0950	0.0915	0.0908	0.0915	
Acetone $\delta_s = 9.77$	0.4143	0.0286	0.0655	0.0684	0.0685	0.0670
	1.3046	0.0949	0.0712	0.0706	0.0711	
Tetrahydrofuran $\delta_s = 9.52$	0.2641	0.019	0.0816	0.0715	0.0716	0.0700
	0.6432	0.0476	0.0722	0.0729	0.0731	
Cyclohexane $\delta_s = 8.18$	0.3667	0.213	0.0576	0.0577	0.0577	0.0565
	0.7388	0.0452	0.0628	0.0603	0.0605	
Cyclohexanone $\delta_s = 9.88$	0.7888	0.0465	0.0589	0.0581	0.0583	0.0560
	1.4000	0.0895	0.0634	0.0621	0.0626	

* Solubility parameter of linseed oil-alkyd = 9.07 (cal/cc)^{1/2}. δ_s = solubility parameter of solvent.

TABLE VI
Comparison of Calculated $[\eta]$ with Extrapolated $[\eta]$ Value of DCO-Alkyd^a in
Different Solvents

Solvent	Concentration (g/dL)	η_{sp}	$[\eta]_D$	$[\eta]_S$	$[\eta]_P$	$[\eta]_E$
Benzene	0.4199	0.0470	0.1106	0.1102	0.1106	0.111
	1.3640	0.1570	0.1113	0.1096	0.1110	
Toluene	0.6007	0.0655	0.1115	0.1067	0.1073	0.1065
	1.4966	0.1676	0.1078	0.1063	0.1078	
Ethyl acetate	0.4722	0.0517	0.0983	0.1076	0.1081	0.1075
	0.8792	0.0976	0.1098	0.1076	0.1085	
Ethyl benzene	0.9203	0.0977	0.1049	0.1029	0.1037	0.1030
	1.5298	0.1664	0.1046	0.1033	0.1047	
Methyl ethyl ketone	0.4963	0.0551	0.1179	0.1090	0.1095	0.1095
	1.0330	0.1172	0.1108	0.1093	0.1103	
Acetone	0.3642	0.0284	0.0745	0.773	0.0774	0.0770
	0.8685	0.0686	0.0771	0.0772	0.0777	
Cyclohexane	0.6153	0.0446	0.0754	0.0714	0.0717	0.0690
	0.9251	0.0673	0.0724	0.0711	0.0716	
Cyclohexanone	0.2527	0.0167	0.0628	0.0657	0.0658	0.0640
	1.5100	0.1135	0.0737	0.0725	0.0732	

^a Solubility parameter of DCO-alkyd = 9.14 (ca./cc)^o.

low concentrations, especially, when specific viscosity of the solution is fairly low (Table III).

Nero and Sikdar¹² tested the applicability of various single point methods by using practical data. The same data are used for calculating the values of $[\eta]$. The analysis of the comparison of $[\eta]_D$, $[\eta]_S$, and $[\eta]_P$ with $[\eta]_E$ indicates that when η_{sp} is low, $[\eta]_P$ values are very close to $[\eta]_E$, for example, they are 0.521, and 0.518, 0.324 and 0.325, 0.428 and 0.429, 0.279 and 0.280, 0.492 and 0.493, 0.238, and 0.239, etc. respectively (Table IV). Even in the case of values obtained from other single-point equations (5) and (6) a similar feature is observed, especially, at fairly low η_{sp} of the solution.

The results obtained by using the reported data indicate that for good applicability of single point equations, concentration of the solute in solution should not be the sole criterion. For example, Deb and Chatterjee used 0.5 and 0.6% concentrations not taking into consideration that in some cases η_{sp} values of the solution exceeded the limits of the applicability of their equation. Solomon and Ciuta also recommended the concentration as the criterion irrespective of the fact that the η_{sp} of one of their polymer solution having 0.26% concentration was as high as 0.676. The analysis of the comparison of calculated $[\eta]$ with the extrapolated $[\eta]$ shows that these equations produce considerably good results when the value of η_{sp} is fairly low. No doubt, the accurate determination of low η_{sp} demands a good setup with automatic controls for measuring the flow time.

SINGLE POINT $[\eta]$ OF ALKYDS IN DIFFERENT SOLVENTS

Generally, the intrinsic viscosity data are used for studying various physical and hydrodynamic parameters related to polymer-solvent interaction. Viscosity measurements conducted on polymer solutions in different sol-

vents are used for generating data for such studies. For the purpose of quick calculation of $[\eta]$ from single concentration, data on the viscosity of alkyd solutions in 10 individual solvents are analyzed for testing the applicability of these equations. The choice of solvents for alkyds was made on the basis of their solubility parameters and that of alkyds.

The values of $[\eta]$ calculated by using eqs. (4)–(6) show the limitations of the single-point method with respect to concentration and η_{sp} of the solution (Tables V and VI). In the case of solvents like benzene, ethyl acetate, and MEK, which have good solvency for the alkyds, negligible differences between $[\eta]_P$ and $[\eta]_E$ values are observed when η_{sp} is fairly low at concentrations below 0.5%. Even in the case of solvents like cyclohexane and cyclohexanone (which are not so good solvents for alkyds) at low concentrations, the differences in the values of $[\eta]_P$ and $[\eta]_E$ are not much. The values of $[\eta]_S$ and $[\eta]_D$ calculated by eqs. (5) and (6) are also found to have fairly good agreement with the values of $[\eta]$ obtained from extrapolation when η_{sp} of the solution is low.

Usually, Huggins' constant K_1 is found to be around 0.35 in the case of good solvent-polymer systems, and the single-point method has better applicability to such systems. For having beforehand information about the compatibility between solvent and polymer, the data on their solubility parameters and on subparameters can be used. The analysis of the viscosity data on alkyd solutions in different solvents also indicates that the single-point methods have good applicability when the solubility parameters of alkyds and that of the solvents are very close to each other. The single-point method is found to have fairly good applicability to alkyd solutions even in solvents which do not have so good compatibility especially when the η_{sp} or concentration is low.

CONCLUSIONS

The basic assumption in deriving the above single-point equations is that the influence of certain parameters becomes negligible at very low concentrations. This is possible only when η_{sp} is fairly low. Hence, for getting good results from single-point methods, concentration should not be the sole criterion as suggested by earlier workers; η_{sp} may also be considered as one of the criteria. In the case of high molecular weight polymers fairly low concentrations should be used for getting low η_{sp} values. The analysis of above data indicates that when η_{sp} is not more than 0.2 the agreement between calculated and extrapolated values of $[\eta]$ is very good. The single-point methods are also found to be applicable to alkyd solutions in different types of solvents.

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