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Determination of intrinsic viscosity of polymeric compounds through a single specific viscosity measurement

Abdel-Azim A. Abdel-Azim*, Aiman M. Atta, Medhat S. Farahat and Wagdy Y. Boutros
Egyptian Petroleum Research Institute, Ahmed El-Zomor St., #1, Nasr City 11727, Cairo, Egypt
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A modified method based on a combination of the Huggins and Schulz–Blaschke equations is proposed which enables the determination of intrinsic viscosity $[\eta]$ from the measurement of a single specific viscosity. The method has been verified for different polymer samples having a wide range of $[\eta]$ values and showed a variation of $< \pm 6 \times 10^{-3}\%$ from the values obtained by Huggins extrapolation method © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Several mathematical equations are available for determining the intrinsic viscosity $[\eta]$ of a polymer solution. The most commonly used equations [Huggins[1], Kraemer[2] and Schulz–Blaschke (S–B)[3]; equations (1)–(3), respectively] require practical data for specific viscosity or relative viscosity for a few concentrations of the polymer in a solvent. These equations are found to be valid at low concentrations, and graphical extrapolation of any one of them is expected to produce more or less the same value of $[\eta]$ for the polymer in a solvent. In doing so a considerable amount of time, effort, and materials are lost in conducting experiments at a series of concentrations and then applying a linear two-parameter approximation to the data. Sometimes, the graphical solutions do not provide very accurate estimation of $[\eta]$.

$$\eta_{sp}/c = [\eta] + k_H[\eta]^2 c \tag{1}$$

$$\frac{\ln\eta_r}{c} = [\eta] - k_K[\eta]^2 c \tag{2}$$

$$\eta_{sp}/c = [\eta] + k_{SB}[\eta]\eta_{sp} \tag{3}$$

where, η_{sp} is the specific viscosity and k_H, k_K and k_{SB} are Huggins, Kraemer's and Schulz–Blaschke viscosity slope constant, respectively. In many polymer–solvent systems it has been proved that $k_H + k_K$ is equal to 0.5.

The value of k_{SB} was found to range between 0.3 and 0.4 and is almost independent on the molecular weight. It is recommended that the concentration of the solution should be such that η_{sp} should exceed the value 0.3–0.5. At very low concentration deviations sometimes occur because of adsorption of macromolecules on the capillary walls of the viscometer, thus reducing the polymer concentration in the measured solution as well as the effective diameter of the capillary. It is therefore not recommended to work with solutions whose $\eta_{sp} < 0.1$.

The least concentration dependence is shown by Martin's equation[4], stated to be applicable to concentrations up to 5%.

$$\log\frac{\eta_{sp}}{c} = \log[\eta]_M + k_M[\eta]_M c \tag{4}$$

Other equations have been also published by Heller[5], Kudlacek[6], Maron and Reznik[7], Elliot et al.[8], Solomon and Ciuta[9] and Solomon and Gottesman[10].

Maron and Reznik[7] showed that when plots are prepared according to equations (1) and (2), they do not extrapolate to the same value of $[\eta]$ and the values of $(k_K + k_K)$ may fall above or below $\frac{1}{2}$. These authors proposed equation (5) as an alternative for measuring the intrinsic viscosity.

$$\frac{\Delta}{c^2} = \frac{[\eta]^2}{2} + (k - \tfrac{1}{3})[\eta]^3 c \tag{5}$$

where

$$\Delta = \eta_{sp} - \ln\eta_r \tag{6}$$

Equation (5) predicts that a plot of Δ/c^2 against c should be a straight line with intercept I given by:

$$I = [\eta]^2/2 \tag{7}$$

from which $[\eta]$ follows as:

$$[\eta] = \sqrt{2I} \tag{8}$$

The intrinsic viscosity, $[\eta]$, is probably the most frequently measured property of high molecular-weight polymers. It is generally determined by measuring the relative viscosities, η_r, 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 kg dm^{-3}). The η_{sp}/c values are then extrapolated to zero concentration, using one of the above mentioned relationships, to obtain $[\eta]$. Plotting of reciprocal values c/η_{sp}, $c/\ln\eta_r$ and their arithmetic mean:

$$\frac{c}{2}\left[\left(\frac{1}{\eta_{sp}}\right) + \left(\frac{1}{\ln\eta_r}\right)\right]$$

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* To whom correspondence should be addressed

against concentration makes the extrapolation more accurate[5]. The intercept on the ordinate axis is then equal to $1/[\eta]$. The Schulz–Blaschke equation, equation (3), is extrapolated by plotting η_{sp}/c against η_{sp}. It is often used for direct calculation of $[\eta]$.

$$[\eta] = \frac{\eta_{sp}/c}{1 + k_{SB}\eta_{sp}} \tag{9}$$

It is apparent that considerable time and effort would be saved if, instead of determining η_r for a series of solutions, a single determination at a known concentration might be used to give $[\eta]$ directly. Several equations have been suggested for a quick determination of the intrinsic viscosity from single-point measurement of viscosity at one concentration. The use of these equations has been derived under the supposition of constancy of k values in equations (1)–(3) and the validity of the $k_H + k_K = 0.5$ relationship. This condition, however, at the same time restricts their applicability.

Several years ago, Martin[11] proposed a method for the determination of intrinsic viscosity of cellulose in cuprammonium or 0.5 M cupriethylenediamine based upon a single viscosity measurement. Recently several workers have proposed and discussed various equations for obtaining $[\eta]$ from a single determination of η_r. These include Solomon and Ciuta[9] and Deb and Chatterjee[12].

Solomon and Ciuta[9] derived their intrinsic viscosity relationship by combining equations (1) and (2). They derived the equation:

$$[\eta] = \frac{1}{c}\sqrt{2(\eta_{sp} - \ln\eta_r)} \tag{10}$$

Equation (11) was proposed by Deb and Chatterjee[12] as an expression for single point determination method of $[\eta]$.

$$[\eta] = \frac{1}{c}[3\ln\eta_r + \tfrac{3}{2}\eta_{sp}^2 - 3\eta_{sp}]^{\frac{1}{3}} \tag{11}$$

Further equations have been derived by other authors, e.g. Solomon and Gottesman[10], Elliott et al.[8], Varma and Sengupta[13], Palit and Kar[14], and Berlin[15].

Extensive studies[16] have shown, however, that for a given polymer–solvent system at a fixed temperature, k_H is a constant. Any appreciable variation in k_H indicates that the polymer is not the 'given polymer' and that some chemical or structural difference is present. Davis[16] carried out a very thorough analysis of capillary viscometry and of the determination of $[\eta]$ by a single-point method, based on the theory of the propagation of errors. Based upon reasonable assumptions, he concluded that if k_H is known to only ±40% $[\eta]$ can be determined to ±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 precision in $[\eta]$ can be achieved with a one-point method, even if there is considerable uncertainty in the value of k_H. Elliott et al.[8], studied the applicability of Solomon and Ciuta's equation (equation (10)) by determining the $[\eta]$ of commercial and experimental samples of polypropylene and polyethylene in decalin. They arrived at the conclusion that the equation of Solomon and Ciuta yields acceptable $[\eta]$ values for these particular polymer–solvent systems.

Recently, on the bases of the Huggins equation (equation (1)) and the Kraemer equation (equation (2)), Ram Mohan Rao and Yaseen[17] proposed a new expression (equation (12)) for calculating $[\eta]$ from a single relative viscosity, η_r, measurement.

$$[\eta] = \frac{1}{2c}[\eta_{sp} + \ln\eta_r] \tag{12}$$

The applicability of this equation was tested by the authors[17] and its validity was tested and compared with other equations by Chee[18].

Solomon and Ciuta[9] have proposed equation (10) for single-point determination of intrinsic viscosity $[\eta]$. These authors arrived at equation (10) experimentally and justify its validity on the grounds that

$$\frac{1}{c}\sqrt{2(\eta_{sp} - \ln\eta_r)}$$

tends to $[\eta]$ as c tends to zero. Narr et al.[19] have derived equation (10) analytically from Huggins' equation[1], and Ibrahim and Elias[20] have derived this by combining Huggins' equation[1] with Kraemer's equation[2]. Deb and Chatterjee[12] have derived another equation of the same type (equation (11)) by eliminating k from Schulz and Blaschke's equation[3]. Palit and Kar[14] have proposed equation (13):

$$[\eta] = \frac{1}{c}\sqrt[4]{4\eta_{sp} - 2\eta_{sp}^2 + \tfrac{4}{3}\eta_{sp}^3 - 4\ln\eta_r} \tag{13}$$

In this work an accurate empirical equation has been derived for determining the intrinsic viscosity from a single specific viscosity measurement.

EXPERIMENTAL

Materials

Benzene was dried over anhydrous $MgSO_4$, filtered and further dried over sodium wire before distillation at atmospheric pressure. The polystyrene sample (PS) of nominal polydispersity index

$$\frac{\bar{M}_w}{\bar{M}_n} = 1.06$$

was obtained from Pressure Chemical Company, Pittsburg, PA, USA. The quoted relative molar mass M was 110 000. Three poly(ethylene oxide) samples were obtained from Aldrich Chemical Co. Ltd. (UK). their quoted relative molar masses M were 1.0×10^5, 3.0×10^5 and 6.0×10^5. These samples are designated here as PEO1, PEO2 and PEO3, respectively. The nominal ratio of weight-to-number-average molecular weights

$$\frac{\bar{M}_w}{\bar{M}_n}$$

for samples PEO1–PEO3 was less than 1.09. Three poly(ethylene glycol) samples were obtained from Aldrich. The quoted relative molar masses, M, for samples PEG1, PEG2 and PEG3, respectively, were 1.5×10^4, 3.5×10^4, and 1.0×10^5.

Density and viscosity

The density of pure benzene was measured dilatometrically at different temperatures as described elsewhere[21,22]. The dilatometer was calibrated with mercury to determine their volumes up to a fixed mark and capillary radii. Details of the preparation of solutions and the measurements of $[\eta]$ have been described elsewhere[23–25]. Viscosities were measured at 293.15 K and 303.15 K in benzene by use of a dilution Ubbelohde viscometer; the flow time was 85 s for pure benzene at 293.15 K and the results are quoted on the basis of Huggins[1] and Kraemer[2] equations.

The viscometer was calibrated with water and the data obtained indicate there was no need to apply end correction to the length of the capillary and kinetic energy correction for this particular viscometer.

RESULTS AND DISCUSSION

The purpose of the following analysis is to examine closely the applicability of the previously mentioned equations and the consistency of the derived values of $[\eta]$ with that obtained by using the Huggins equation. In this respect the intrinsic viscosities of PEO1, PEO2, PEO3 and PEG3 were determined at 293.15 K and 303.15 K by applying the above proposed equations. The $[\eta]$ of PEG1, PEG2 and PS were also measured at 303.15 K. The data for $[\eta]$ for these polymers at different concentrations are listed in *Tables 1* and *2*.

In an exercise of the analysis of practical viscosity data considerable variation was observed in the values of $[\eta]$ calculated by use of different one-point measurement equations. The data listed in *Tables 1 and 2* show that Solomon and Ciuta's equation affords $[\eta]$ values in good agreement with $[\eta]$ obtained from Huggins' plot. It can be seen from these data that Deb and Chatterjee method of calculation gives higher values of $[\eta]$ than those obtained by Solomon and Ciuta's method. The highest values of $[\eta]$ are obtained when Palit and Kar's method is used. It can be seen also that the values obtained by the last two methods are concentration-dependent. In these two methods the values of $[\eta]$ increases with increasing the concentration and the resultant difference between the obtained value and the value of $[\eta]$ derived from Huggins' plot increases with increasing the molecular weight of the polymer. From these data one could at best conclude that Solomon and Ciuta's equation gives $[\eta]$ in better agreement with the extrapolated $[\eta]$ from Huggins' equation than those obtained from either Deb and Chatterjee's equation or Palit and Kar's equation. Gillespie and Hulme[26] have carried out an analysis of the Solomon and Ciuta equation and found that it should give results in agreement with the Huggins equation when k_H in the latter is $\frac{1}{3}$. Nero and Sikdar[27] preferred Solomon and Ciuta's equation to other methods as they felt it had a means of testing the correctness of the single-point $[\eta]$ value.

Solomon and ciuta proposed their equation for obtaining the intrinsic viscosity of a polymer by the measurement of the viscosity of the polymer in solution at a single concentration. These authors arrived at equation (10) experimentally. This equation can be derived analytically from the Huggins relationship (equation (1)). The derivation starts with rearrangement of equation (1) as in equations (14a), (14b) and (14c):

$$\eta_{sp} = [\eta]c + k_H[\eta]^2c^2 \quad (14a)$$

$$\eta_r = 1 + [\eta]c + k_H[\eta]^2c^2 \quad (14b)$$

Table 1 Intrinsic viscosity of PEO samples derived at different concentrations and temperatures using different equations

Polymer	Temp. (K)	Conc. × 10^3 (kg dm^{-3})	$[\eta]$*	η_{sp}	Equation: Solomon and Ciuta	Deb and Chatterjee	Palit and Kar
	293.15	7.50	94.6	0.8916	95.07	100.63	104.12
		5.77		0.6529	95.04	99.34	102.01
		3.57		0.3789	95.08	97.76	99.39
PEO1	303.15	2.59		0.2664	94.92	96.86	98.04
		7.13	98.3	0.8785	98.78	104.49	108.07
		5.55		0.6521	98.71	103.16	105.93
		4.16		0.4689	98.75	102.11	104.17
		3.12		0.3406	98.77	101.29	102.84
		2.17		0.2299	98.77	100.52	101.59
	293.15	3.00	208.9	0.7674	209.70	220.56	227.33
		2.14		0.5190	209.97	217.76	222.57
		1.25		0.2855	209.69	214.25	217.03
PEO2		1.00		0.2246	209.69	213.34	215.56
	303.15	3.11	221.4	0.8587	222.22	234.84	242.74
		2.48		0.6592	222.95	233.11	239.43
		1.66		0.4152	222.04	228.81	232.97
		1.18		0.2868	222.06	227.93	230.91
	293.15	2.08	357.1	0.9455	359.76	381.84	395.72
		1.79		0.7853	358.34	377.24	389.04
		1.47		0.6250	359.31	374.96	384.67
		1.19		0.4906	359.33	372.03	379.86
PEO3		0.71		0.2789	361.29	368.97	373.66
	303.15	1.87	363.0	0.8472	365.46	385.98	398.83
		1.67		0.7362	363.75	381.93	393.27
		1.25		0.5273	364.50	378.22	386.69
		1.07		0.4429	364.95	376.74	383.99
		0.71		0.2834	366.67	374.59	379.42

$[\eta]$* obtained by Huggins graphical extrapolation

Table 2 Intrinsic viscosity of PEG and PS samples derived at different concentrations and temperatures using different equations

Polymer	Temp. (K)	Conc. $\times 10^3$ (kg dm^{-3})	$[\eta]^*$	η_{sp}	Equation		
					Solomon and Ciuta	Deb and Chatterjee	Palit and Kar
PEG1	303.15	22.28	33.92	0.9632	34.10	36.23	37.56
		16.34		0.6651	34.10	35.66	36.64
		11.14		0.4294	34.10	35.17	35.83
		7.66		0.2844	34.10	34.84	35.29
PEG2	303.15	13.96	53.10	0.9402	53.36	56.62	58.66
		11.81		0.7691	53.37	56.14	57.86
		9.03		0.5624	53.38	55.51	56.82
		6.14		0.3645	53.38	54.83	55.72
		4.39		0.2527	53.32	54.36	54.99
PEG3	293.15	10.71	67.78	0.9171	68.14	72.22	74.78
		8.33		0.6797	68.14	71.33	73.31
		5.77		0.4460	68.10	70.31	71.67
		3.41		0.2505	68.09	69.40	70.20
	303.15	10.09	70.10	0.8881	70.43	74.54	77.12
		7.57		0.6316	70.41	73.50	75.42
		5.05		0.3987	70.38	72.45	73.72
		3.03		0.2286	70.36	71.60	72.36
PS	303.15	9.87	57.4	0.6811	57.61	60.31	61.99
		7.05		0.4629	57.61	59.54	60.74
		4.94		0.3118	57.54	58.90	59.73
		3.53		0.2171	57.54	58.51	59.10

$[\eta]^*$ obtained by Huggins graphical extrapolation

$$\ln \eta_r = \ln\{1 + [\eta]c + k_H[\eta]^2c^2\} \tag{14c}$$

Expanding into series, neglecting terms in c^3 and higher, and rearranging, leads to:

$$\ln \eta_r = [\eta]c + [\eta]^2\left(k_H - \tfrac{1}{2}\right)c^2 \tag{15}$$

Subtracting equation (15) from equation (14a), one obtains:

$$\eta_{sp} - \ln\eta_r = \tfrac{1}{2}[\eta]^2c^2 \tag{16}$$

Transposing, equation (16) leads to equation (10) (Solomon and Ciuta's equation). It is important to realize, however, that the validity of equation (10) for any polymer–solvent system depends only on the validity of the Huggins' equation for that system, since equation (10) is derived therefrom. On the other hand, use of equation (10) in conjunction with the classical three-point determination and graphical extrapolation is sufficient to establish whether the Huggins' equation applies for a given polymer–solvent system. If the $[\eta]$ obtained by graphical extrapolation agrees with the $[\eta]$ obtained by use of equation (10) then the Huggins' relation applies. Equation (15) also shows that for values of $k_H > 1/2$, plots of $\ln\eta_r/c$ against c (used in the determination of inherent viscosities) will have a positive rather than the usual negative slope.

The agreement between the values of $[\eta]$ obtained from the equations proposed by Huggins and by Solomon and Ciuta furnished support for the previous selection of Huggins' equation for determining the intrinsic viscosity in this investigation.

Hereinafter we propose a modified method based on the combined Huggins and Schulz–Blaschke's equation which enables the calculation of $[\eta]$ from the measurement of a single specific viscosity. In this respect the new equation is derived as follows.

Huggins' equation $\eta_{sp}/c = [\eta] + k_H[\eta]^2c$ can be rearranged to the form of equation (17):

$$\frac{\eta_{sp}}{[\eta]c} = 1 + k_H[\eta]c \tag{17}$$

If the value of

$$[\eta] = \frac{\eta_{sp}/c}{1 + k_{SB}\eta_{sp}}$$

(Schulz and Blaschke's equation) is substituted in equation (17) then equation (18) is obtained.

$$\frac{\eta_{sp}}{[\eta]c} = 1 + k_H\frac{\eta_{sp}}{1 + k_{SB}\eta_{sp}} \tag{18}$$

Rearrangement of equation (18) yields equation (19)

$$\frac{1}{[\eta]} = \frac{c}{\eta_{sp}} + \frac{k_H\eta_{sp}c}{\eta_{sp}(1 + k_{SB}\eta_{sp})} \tag{19}$$

Then

$$\frac{1}{[\eta]} = \frac{c}{\eta_{sp}} + \frac{k_Hc}{1 + k_{SB}\eta_{sp}} \tag{20}$$

which leads to

$$\frac{1}{[\eta]} = \frac{c(1 + k_{SB}\eta_{sp}) + k_H\eta_{sp}c}{\eta_{sp}(1 + k_{SB}\eta_{sp})} \tag{21}$$

$[\eta]$ is calculated from the reciprocal of equation (21) according to equation (22) if k_{SB} and k_H are taken as constant values for the polymer–solvent system:

$$[\eta] = \frac{\eta_{sp} + k_{SB}\eta_{sp}^2}{c + k_{SB}\eta_{sp}c + k_H\eta_{sp}c} \tag{22}$$

Table 3 Intrinsic viscosity and viscosity slope constant at 293.15 K and 303.15 K derived from Huggins and Schulz–Blaschke equations for different polymer–benzene systems

Temp. (K)	Polymer	Method of Extrapolation			
		Huggins		Schulz–Blaschke	
		$[\eta]$	k_H	$[\eta]$	k_{SB}
293.15	PEO1	94.60	0.3605	96.48	0.263
	PEO2	208.90	0.3572	212.06	0.271
	PEO3	357.10	0.3642	365.19	0.259
	PEG3	67.78	0.3606	69.08	0.263
303.15	PEO1	98.30	0.3594	100.07	0.266
	PEO2	221.40	0.3608	225.85	0.263
	PEO3	363.00	0.3607	369.95	0.264
	PEG1	33.92	0.3623	34.66	0.259
	PEG2	53.10	0.3613	54.16	0.262
	PEG3	70.10	0.3596	71.32	0.263
	PS	57.40	0.3551	58.15	0.276

Table 4 Statistical analysis for the viscosity slope constants derived from Huggins and Schulz–Blaschke equations for different polymer–benzene systems

Statistical parameter	Statistical analysis data for		
	k_H (PEO)	k_H (PEG)	k_{SB} (all polymers)
a.d. $\times 10^3$	1.72	0.85	3.5
a.d. (mean) $\times 10^3$	0.769	0.425	1.055
s $\times 10^3$	2.545	1.139	4.89
s (mean) $\times 10^3$	1.138	0.569	1.47
Confidence limit	0.3605 ± 0.00315	0.3609 ± 0.0018	0.2648 ± 0.00328

Confidence limit are based on 95% confidence level

It has been reported[1] that k_H in equation (17) is constant for a large number of polymer solvent systems and Khan et al.[28] reported a value of 0.28 for k_{SB}. However, hereinafter statistical analysis is performed for the measured values of k_H and k_{SB} for different polymer–benzene systems to confirm that they are constant in the systems studied. The specific viscosity–concentration relationships for all polymer–benzene systems are based on the Huggins equation and the Schulz–Blaschke equation.The $[\eta]$ values obtained from the Huggins and Schulz–Blaschke equations in conjunction with both k_H and k_{SB} are tabulated in *Table 3* and the statistical analysis data of these values are illustrated in *Table 4*.

The average deviation (*a.d.*), average deviation from the mean (*a.d.(mean)*), standard deviation (*s*) and standard deviation of the mean [*s(mean)*] of the measurements of each set of data (k_H and k_{SB}) were calculated according to equations (23)–(26).

$$a.d. = \frac{\left(\sum \left| x_i - \bar{x} \right|\right)}{N} \tag{23}$$

where $\bar{x}$ = the mean of the measurements

$$\frac{\sum x_i}{N},$$

x_i = the individual measurements, and N = the number of measurements.

$$a.d.(mean) = \frac{a.d.}{\sqrt{N}} \tag{24}$$

$$s = \frac{\sqrt{\sum (x_i - \bar{x})^2}}{(N-1)} \tag{25}$$

$$s(mean) = \frac{s}{\sqrt{N}} \tag{26}$$

Calculation of the standard deviation for a set of data provides an indication of the precision inherent in a particular procedure or analysis. But unless there are a large number of data, it does not by itself give any information about how close the experimentally determined mean $\bar{x}$ might be to the true mean value. Statistical theory, though, enables us to estimate the range within which the true value might fall, within a given probability, defined by the experimental mean and the standard deviation. The likelihood that the true value falls within the range is called the ***confidence level***, usually expressed as a percent. The confidence limit is given by equation (27):

$$\text{Confidence limit} = \bar{x} \pm \frac{ts}{\sqrt{N}} \tag{27}$$

where t is a statistical factor that depends on the number of degrees of freedom and the confidence level desired.

The data given in *Table 4* reveal that k_{SB} is constant for all polymer–benzene systems under investigation and equals 0.2648 ± 0.00328. Although the value of k_H is constant for each system, regardless of the temperature, it varies from system to system. This finding agrees with previous reports[1,28] of the constancy of k_H for many polymer–solvent systems. Since k_H is constant for each of the

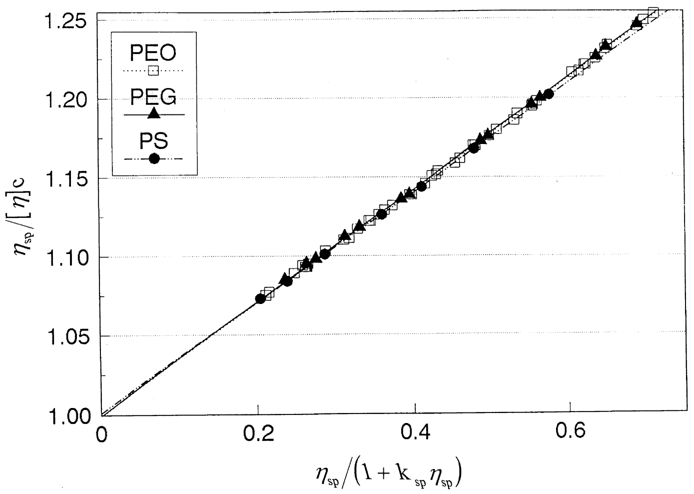

Figure 1 Plot according to equation (18) for different polymers at 293.15 K and 303.15 K

Table 5 Least-squares analysis for different polymer–benzene systems

System	Intercept	Slope (k_H)	r^2
PEO–benzene	0.999	0.3559	0.9995
PEG–benzene	0.999	0.3568	0.9997
PS–benzene	1.000	0.3475	0.9999

polymer–benzene systems studied, the plot of

$$\frac{\eta_{sp}}{[\eta]c} \text{ against } \frac{\eta_{sp}}{1+0.2648\eta_{sp}},$$

according to equation (18), should give a straight line of slope k_H for each polymer–solvent system and a unique intercept equal to unity. This was tested by plotting the corresponding X–Y values for each polymer–benzene system regardless of molecular weight of the polymer, the temperature of the viscosity measurements and the concentration of the polymer solution. The plot illustrated in *Figure 1* indicates that all calculated values for each polymer–benzene system lie on the same straight line. Since the slopes of these lines are quite close, these lines are difficult to distinguish. Accordingly, the least-squares analysis of these lines are presented in *Table 5*.

The goodness of fit as indicated by r^2 and the intercepts which are almost equal to unity reflect the validity of equation (18). The slight difference between the intercepts and unity and the difference between the slopes and k_H obtained by statistical analysis may be reduced when more k_H values are tested and hence the standard deviation

Table 6 Statistical analysis of [η] obtained for the polymers studied at various concentrations using different equations at different temperatures

Polymer	Temp. (K)	Statistical parameter	Statistical analysis for the [η] data of:		
			Solomon and Ciuta	equation (9)	equation (28)
PEO1	293.15	S	0.06	0.17	0.07
		Conf. limit	95.05 ± 0.05	96.36 ± 0.14	94.36 ± 0.06
	303.15	S	0.05	0.16	0.12
		Conf. limit	98.74 ± 0.04	100.10 ± 0.12	98.04 ± .09
PEO2	293.15	S	0.24	0.40	0.36
		Conf. limit	209.66 ± 0.22	212.58 ± 0.35	208.19 ± 0.33
	303.15	S	0.36	0.42	0.45
		Conf. limit	222.59 ± 0.30	225.76 ± 0.35	220.92 ± 0.38
PEO3	293.15	S	0.98	0.84	1.23
		Conf. limit	359.27 ± 0.75	364.23 ± 0.65	356.56 ± 0.95
	303.15	S	1.33	1.29	1.43
		Conf. limit	365.11 ± 1.23	370.31 ± 1.19	362.38 ± 1.32
PEG1	303.15	S	0.006	0.06	0.03
		Conf. limit	34.10 ± 0.006	34.57 ± 0.06	33.85 ± 0.03
PEG2	303.15	S	0.02	0.10	0.05
		Conf. limit	53.36 ± 0.02	54.08 ± 0.08	52.98 ± 0.04
PEG3	293.15	S	0.03	0.11	0.07
		Conf. limit	68.09 ± 0.003	69.03 ± 0.09	67.62 ± 0.06
	303.15	S	0.04	0.13	0.06
		Conf. limit	70.39 ± 0.04	71.34 ± 0.12	69.88 ± 0.06
PS	303.15	S	0.04	0.12	0.08
		Conf. limit	57.59 ± 0.04	58.38 ± 0.11	57.19 ± 0.07

becomes more precise. It is of interest to mention that the values of k_H obtained from *Figure 1* are derived from a large number of points (many concentrations, different temperatures and different polymer–benzene systems). However the approximation of the values of k_H listed in *Table 5* to the second decimal point yields values of k_H almost the same as that obtained by the statistical analysis. Accordingly, the values of 0.3559, 0.3568 and 0.3475 are assigned here for PEO–benzene, PEG–benzene and PS–benzene systems, respectively. These values were incorporated in equation (28) for the sake of testing the validity of this equation as a new method for measuring the $[\eta]$ via a single specific viscosity measurement.

$$[\eta] = \frac{\eta_{sp}(1 + 0.2648\eta_{sp})}{c + \eta_{sp}(0.2648c + k_H c)} \tag{28}$$

In this respect, the specific viscosity values, measured at various concentrations for each polymer–benzene system, were used to derive the corresponding $[\eta]$ via Solomon & Ciuta's equation, equations (9) and (28). It was found that the equations tested afford almost constant values of intrinsic viscosity over all the concentration range of the examined polymer–solvent systems. The values obtained were statistically analysed to determine the standard deviation and the confidence limit for each set of measurements. The statistical data for all the polymers studied at different temperatures are presented in *Table 6*. Upon comparing the obtained $[\eta]$ values listed in *Table 6* with that obtained via the Huggins extrapolation procedure (*Table 3*) the following observations and conclusions can be drawn:

- The standard deviation of the intrinsic viscosities calculated for different concentrations using Solomon and Ciuta's equation is always less than the standard deviations of the data obtained by use of the other two equations.
- Equation (28) affords a confidence range of intrinsic viscosity for each system, within which or very close to it, the true value ($[\eta]_H$) is located, within 95% confidence probability. The range afforded by Solomon-Ciuta's equation and Schulz–Balschke's equation are always higher than $[\eta]_H$.

Accordingly, it is legitimate to state that the newly proposed equation (equation (28)) is more reliable than other equations reported in the literature for estimating the intrinsic viscosity from a single measurement of specific viscosity since the obtained $[\eta]$ values for all tested polymers at different temperatures showed a variation of $< \pm 6 \times 10^{-3}\%$ from the values obtained by Huggins extrapolation method.

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