A Critical Evaluation of the Single-Point Determination of Intrinsic Viscosity

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Synopsis

The general validity of four single-point methods for intrinsic viscosity ($[\eta]$) determination is verified to be unacceptable even for dilute polymer solutions. Also, a direct method based on a truncated version of Huggins equation is shown to be less practical in that it involves advanced experimentation and is valid only at sufficiently low concentrations. In view of the shortcoming and sophistication of the above procedures, an effective approach is introduced to resolve these problems. This novel computation expresses the Huggins coefficient in terms of $[\eta]$, and the associated equations are calibrated against the polymer system of interest. This procedure is tested using various polymer solutions with results compatible with those acquired by other means. The advantage of the proposed technique is discussed.

INTRODUCTION

The intrinsic viscosity ($[\eta]$) of a polymer in solution is a useful parameter for polymer characterization. As such, a number of procedures[1,2] has been suggested to determine this important quantity. Usually, the intrinsic viscosity is computed by the Huggins equation, which is operative below the overlap concentration,[3] given by

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

where η_{sp} is the specific viscosity of a polymer solution with concentration C and k is the Huggins coefficient. Accordingly, a plot of η_{sp}/C vs. C would give a straight line whose intercept and slope result in $[\eta]$ and k, respectively. Recently, several attempts have been made to estimate $[\eta]$ directly from a single measurement of η_{sp} at an appropriate C. This paper examines critically the general validity of these methods, and a novel approach to overcome their limitations is presented.

RESULTS AND DISCUSSION

The following expressions for single point determinations of $[\eta]$ have been developed respectively by Solomon and Ciuta,[4] Ram Mahan Rao and Yaseen,[5] and Deb and Chatterjee[6]:

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

$$[\eta] = (1/2C)(\eta_{sp} + \ln \eta_r) \tag{3}$$

$$[\eta] = (1/C)(3 \ln \eta_r + 1.5\eta_{sp}^2 - 3\eta_{sp})^{1/3} \tag{4}$$

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where η_r is the relative viscosity. Using a semiempirical model for the hydrodynamic volume of solvated polymer, Rudin and Wagner[7] have derived

$$[\eta] = \frac{\phi(1.31\rho - 2.5C)}{C\rho(0.524 - \phi)} \tag{5}$$

where ρ is the density of polymer and ϕ is the volume fraction of swollen polymer in solution given by

$$\phi = \frac{0.524C\epsilon_0}{0.524\rho + C(\epsilon_0 - 1)} \tag{6}$$

with

$$\epsilon_0 = \frac{\rho[\eta]}{2.5} \tag{7}$$

Equation (5) is applied to solve for $[\eta]$ in conjunction with the Ford's relationship

$$\eta_r = \left(1.0 - 2.5\phi + 11.0\phi^5 - 11.5\phi^7\right)^{-1} \tag{8}$$

This rather complex algorithm may be considerably simplified by converting eq. (5) to the following form based on two appropriate approximations:

$$[\eta] = (\eta_{sp}/C)(1 + 0.24\eta_{sp})^{-1} \tag{9}$$

for $[\eta] \gg 2.5/\rho$ and $\eta_{sp}(= \eta_r - 1) \ll 1.0$.

Now we proceed to compare eq. (1) with (2)–(4) and (9). To this end, eq. (1) is expanded to a series form

$$[\eta]C = \eta_{sp}\left(1 - k\eta_{sp} + 2k^2\eta_{sp}^2 - 5k^3\eta_{sp}^3 + \cdots\right) \tag{10}$$

Analogously, eqs. (2)–(4) and (9) are respectively recast to

$$[\eta]C = \eta_{sp}\left(1 - \frac{1}{3}\eta_{sp} + \frac{7}{36}\eta_{sp}^2 - \frac{1}{80}\eta_{sp}^3 + \cdots\right) \tag{11}$$

$$[\eta]C = \eta_{sp}\left(1 - \frac{1}{4}\eta_{sp} + \frac{1}{6}\eta_{sp}^2 - \frac{1}{4}\eta_{sp}^3 + \cdots\right) \tag{12}$$

$$[\eta]C = \eta_{sp}\left(1 - \frac{1}{4}\eta_{sp} + \frac{11}{80}\eta_{sp}^2 - \frac{1}{15}\eta_{sp}^3 + \cdots\right) \tag{13}$$

$$[\eta]C = \eta_{sp}\left(1 - 0.24\eta_{sp} + 5.76 \times 10^{-2}\eta_{sp}^2 - 1.38 \times 10^{-2}\eta_{sp}^3 + \cdots\right) \tag{14}$$

all for $\eta_{sp} < 1$. Clearly, eqs. (11)–(14) are the special cases of eq. (10) with the coefficient k being equal to 0.33, 0.25, 0.25, and 0.24, respectively, when the

TABLE I
The k' Values at Various η_{sp} for the Four Single-Point Methods

No.	η_{sp}	Eq. (2)	Eq. (3)	Eq. (4)	Eq. (5)[a]
1	0.005	0.333	0.250	0.249	0.240
2	0.010	0.334	0.250	0.245	0.240
3	0.050	0.335	0.248	0.249	0.240
4	0.100	0.336	0.246	0.249	0.242
5	0.200	0.338	0.242	0.247	0.247
6	0.400	0.343	0.234	0.245	0.255
7	1.000	0.353	0.214	0.239	0.272
8	2.000	0.365	0.188	0.231	0.285
9	3.000	0.373	0.168	0.224	0.292
10	5.000	0.384	0.139	0.214	0.298

[a] For $[\eta] \gg 2.5/\rho$, eq. (5) approximates to $[\eta]C = 1.31\phi/(0.524 - \phi)$, where ϕ is readily obtained by the Newton iterative method using eq. (8).

second and higher power terms of η_{sp} in the series are insignificant for low η_{sp}. However, at higher η_{sp} eq. (1) is rearranged to

$$k = \frac{\eta_{sp} - [\eta]C}{[\eta]C} \tag{15}$$

In the present context, the coefficient k in eq. (15) is replaced by k' if the product $[\eta]C$ refers to the one-parameter models, that is eqs. (2)–(5). Implicitly, the new coefficient k' is solely dependent on η_{sp} or η_r.

Table I shows the results obtained by eq. (15) for the four single-point methods as a function of η_{sp}. Obviously, these simplified expressions are by no means equivalent to eq. (1), unless the coefficients k' and k are identical, thus denying the universality of the former. Theoretically, their predictions of $[\eta]$ are susceptible to C, particularly at high η_{sp}. However, in practice, they are quite comparable with an average $k' = 0.28 \pm 0.07$ as $\eta_{sp} \leq 1$. This is substantiated by the consistencies of the $[\eta]$ data on various polymer solutions obtained by these methods.[5]

A general solution to the present problem is possible by using

$$[\eta] = \eta_{sp}/C \tag{16}$$

However, eq. (16) is subject to two constraints: (1) the k term in eq. (1) must be negligibly small in comparison with $[\eta]$, that is,

$$\epsilon = k\eta_{sp} \ll 1 \tag{17}$$

and (2) the experimental uncertainty in $[\eta]$ should be tolerable in the sense that

$$[\Delta] = \sigma_{[\eta]}/[\eta] \ll 1 \tag{18}$$

where $\sigma_{[\eta]}$ is the standard deviation of $[\eta]$ estimated by eq. (16). Surely, the index Δ depends primarily on the experimental technique utilized to monitor η_r, as elaborated below.

The variance of $[\eta]$ denoted by $\mathrm{Var}([\eta])$ arising from the random errors in $[\eta]$ determinations via eq. (16) is given by

$$\mathrm{Var}([\eta]) = [\eta]^2\left[\frac{\mathrm{Var}(C)}{C^2} + \frac{\mathrm{Var}(\eta_{\mathrm{sp}})}{\eta_{\mathrm{sp}}^2}\right] \tag{19}$$

where $\mathrm{Var}(C)$ and $\mathrm{Var}(\eta_{\mathrm{sp}})$ are the variances of C and η_{sp}, respectively. Also we have

$$\mathrm{Var}(C) = C^2\left[\frac{\mathrm{Var}(m)}{m^2} + \frac{\mathrm{Var}(V)}{V^2}\right] \tag{20}$$

where $\mathrm{Var}(m)$ and $\mathrm{Var}(V)$ are the variances of the mass of polymer (m) and volume of solution (V), respectively. Basically, there are two distinct techniques for measuring η_{sp}. These are the Ubbelohde viscometry (UV) and the newly invented differential viscometry (DV).[8] The equations pertaining to UV and DV are respectively

$$\eta_{\mathrm{sp}} = (t/t_0) - 1 \tag{21}$$

$$\eta_{\mathrm{sp}} = 4\,\Delta P/(P_i - 2\,\Delta P) \tag{22}$$

where t and t_0 are the flow times of the polymer solution and pure solvent, respectively, P_i is the inlet pressure to a bridge network of four capillaries, and ΔP is the difference in the equilibrium pressure drops across two capillaries whose reservoirs are filled with the sample solution and solvent. For dilute solutions, eqs. (21) and (22) respectively lead to[2]

$$\mathrm{Var}(\eta_{\mathrm{sp}}) = \left(2 + 2\eta_{\mathrm{sp}} + \eta_{\mathrm{sp}}^2\right)\frac{\mathrm{Var}(t_0)}{t_0^2} \tag{23}$$

$$\mathrm{Var}(\eta_{\mathrm{sp}}) = \eta_{\mathrm{sp}}^2\left(1 + \frac{\eta_{\mathrm{sp}}}{2}\right)^2\left[\frac{\mathrm{Var}(P_i)}{P_i^2} + \frac{\mathrm{Var}(\Delta P)}{\Delta P^2}\right] \tag{24}$$

where $\mathrm{Var}(t_0)$, $\mathrm{Var}(P_i)$, and $\mathrm{Var}(\Delta P)$ are the variances of t_0, P_i, and ΔP, respectively. Combining eqs. (18)–(21) and (23) yields Δ, which is the square root of $\mathrm{Var}([\eta])/[\eta]^2$ [eq. (19)]:

$$\Delta = \left(A + B\eta_{\mathrm{sp}}^2\right)^{1/2}/\eta_{\mathrm{sp}} \tag{25}$$

where

$$A = 2\left(\sigma_{t_0}/t_0\right)^2 \tag{25a}$$

$$B = \mathrm{Var}(C)/C^2 = \left(\sigma_m/m\right)^2 + \left(\sigma_V/V\right)^2 \tag{25b}$$

with σ_{t_0}, σ_m, and σ_V being the standard deviations (square roots of variances) of t_0, m, and V, respectively. Interestingly, while ϵ is directly proportional to

TABLE II
Values of Viscometric Parameters Computed at $k = 2/3$

C (g/dL)	No.	$[\eta]^*$ (dL/g)[a]	η_{sp}[b]	$[\eta]$[c]	Δ[d] (%)	ϵ (%)
0.010	1	0.030	0.0003	0.030	47.1	0
	2	0.100	0.0010	0.100	14.2	0
	3	0.300	0.0030	0.300	4.8	0
	4	0.500	0.0050	0.500	3.0	0
	5	0.800	0.00804	0.804 (0.802)[e]	2.0	0.5
	6	1.000	0.0101	1.010 (1.003)	1.7	1.0
	7	2.000	0.0203	2.030 (2.013)	1.2	1.5
	8	3.000	0.0306	3.060 (3.030)	1.1	2.0
	9	5.000	0.0517	5.170 (5.083)	1.0	3.4
	10	10.000	0.1067	10.670 (10.333)	1.0	6.7
0.100	1	0.010	0.0010	0.010	14.1	0
	2	0.030	0.0030	0.030	4.7	0
	3	0.050	0.0050	0.050	2.8	0
	4	0.100	0.0101	0.101 (0.100)[e]	1.4	1.0
	5	0.300	0.0306	0.306 (0.303)	0.5	2.0
	6	0.500	0.0517	0.517 (0.508)	0.3	3.3
	7	0.800	0.0843	0.843 (0.821)	0.2	5.4
	8	1.000	0.1067	1.067 (1.033)	0.2	6.7

[a] True value of $[\eta]$.
[b] Obtained from eq. (1) based on $[\eta]^*$.
[c] Obtained from eq. (16).
[d] Based on $\sigma_m = 1 \times 10^{-4}$ g, $m = C$ g, $\sigma_V = 0.1$ mL, $V = 100$ ml, $\sigma_{t_0} = 0.01S$ and $t_0 = 100.0S$.
[e] Values in the parentheses are based on $k = 1/3$.

η_{sp} [eq. (17)], eq. (25) indicates that Δ is inversely related to η_{sp} at low η_{sp}. This means that the foregoing criteria confine eq. (16) to an appropriate range of C. Table II illustrates the validity of this simple procedure at a typical experimental error structure achievable by employing the conventional analytical technique for sample preparation and the light sensor for flow time measurements. Here the constant k is taken as 2/3, a value close to the theoretical figure for coils,[9] and is larger than the k values for most polymer solutions.[10,11] Practically, $[\eta]$ is not very sensitive to k as demonstrated in Table II. For high molecular weight polymer samples, specifically with $[\eta]$ ranging from 0.50 to 5.00 dL/g, the concentration in the order of 0.010 g/dL is workable as inferred from Table II. However, more concentrated polymer solutions with C equal to or larger than 0.10 g/dL are required for $[\eta]$ below 0.50 dL/g. This is relevant to the findings from the viscometric studies on a semipolymerized linseed oil–pentaerytriolphthalate and a semipolymerized castor oil–pentaerytritolphthalate, both with $[\eta] < 0.12$ dL/g.[5] Hence, the information displayed in Table II is essential for selecting the optimum concentration for a particular $[\eta]$ measurement by this single-point method.

For the DV, we assume $\sigma_{P_i}/P_i = \sigma_{\Delta P}/\Delta P$,[8] where σ_{P_i} and $\sigma_{\Delta P}$ are the standard deviations of P_i and ΔP, respectively. It follows that eqs. (18)–(20), (22), and (24) result in

$$\Delta = \left[B + 2(1 + \eta_{sp}/2)^2(\sigma_{P_i}/P_i)^2\right] \qquad (26)$$

At the infinite dilution, eqs. (25) and (26), respectively, reduce to

$$\Delta = \sqrt{2}\,\sigma_{t_0}/(t_0[\eta]C) \tag{27}$$

$$\Delta = \sigma_C/C \tag{28}$$

Under this particular condition, eq. (17) vanishes. Equations (27) and (28) imply that the DV is superior to the UV for $[\eta] < 1.4$ dL/g, beyond which the latter technique is favorable, if $\sigma_C = 1 \times 10^{-4}$ g/dL and $\sigma_{t_0}/t_0 = 1 \times 10^{-4}$. The performance of DV has been justified to be satisfactory at least for polystyrene and polyethylene solutions,[8] using eq. (16). In fact, the success of this particular method has been exploited to monitor the molecular weight distribution of polymer by incorporating a DV on line with a size-exclusion chromatograph as the viscosity detector.[12] Perhaps, the main disadvantage regarding the utility of eq. (16) is that it involves sophisticated instrumentation and delicate experimental technique. To eliminate this shortcoming, we further perform the following analyses.

It has been postulated that the product $k[\eta]^2$ is a linear function of $[\eta]$:

$$k[\eta]^2 = a + b[\eta] \tag{29}$$

where a and b are empirical constants.[13] Substituting eqs. (29) into (1) yields

$$[\eta] = \frac{\eta_{sp} - aC^2}{C(1 + bc)} \tag{30}$$

Hence, $[\eta]$ can be estimated directly if a and b are predetermined. Since the coefficients a and b are of opposite signs,[14] negative k is obtained when $[\eta]$ is smaller or larger than the ratio a/b, depending on the sign of a. This prompts us to propose empirically

$$\ln k = m + n \ln[\eta] \tag{31}$$

where m and n are constants. Combining eqs. (1) and (31) renders

$$\ln[\eta] = \left(\frac{1}{2 + n}\right)(\ln \alpha - m) \tag{32}$$

where

$$\alpha = \frac{\eta_{sp}}{C^2} - \frac{[\eta]}{C} \tag{32a}$$

Equation (32) may be solved by the Newton iterative method, using the recursion formula

$$[\eta]'' = [\eta]' - \frac{C[\eta]'\alpha'[m - \ln \alpha' + (2 + n)\ln[\eta]']}{[\eta]' + (2 + n)C\alpha'} \tag{33}$$

TABLE III
Comparison of $[\eta]$ Values Obtained by Various Methods for Polystyrene–Acrylonitrile Copolymer Samples in Butanone at 30°C[a]

No.	C (g/dL)	η_{sp}	$[\eta]$ (dL/g) [eq. (1)]	$[\eta]$ (dL/g) (Khan–Bhargava)	$[\eta]$ (dL/g) [eq. (30)]
1	0.3155	0.2309	0.675	0.67	0.661
2	0.2653	0.2160	0.750	0.75	0.736
3	0.6580	0.6350	0.785	0.76	0.758
4	0.5474	0.5879	0.800	0.82	0.853
5	0.7325	0.8277	0.825	0.83	0.842
6	0.4017	0.4507	0.900	0.93	0.931
7	0.5560	0.9091	1.31	1.23	1.22

[a] The values of a and b are respectively equal to -0.39 and 0.93.

where

$$\alpha' = \frac{\eta_{sp}}{C^2} - \frac{[\eta]'}{C}$$

Here $[\eta]'$ and $[\eta]''$ are the two successive approximations of $[\eta]$. Equation (33) converges readily to a root of $[\eta]$ by setting the first approximation of $[\eta] < \eta_{sp}/C$. Hence, $[\eta]$ is accessible if m and n are known.

Khan and Bhargava[15] have studied the viscometric behavior of a series of styrene–acrylonitrile copolymer samples in butanone at 30°C, with results leading to the constants a, b, m, and n equal to -0.39, 0.93, -0.625, and 0.091, respectively. Because the standard errors of estimate of k (σ_k) for eqs. (29) and (31) are computed to be 0.075 and 0.084, respectively, eq. (30) is preferred in this particular case. Table III lists a number of the single-point measurements of η_{sp} for the foregoing polymer solutions after Khan and Bhargava,[15] who have also put forward a unique graphical method to evaluate the $[\eta]$. The value of $[\eta]$ resulted from eq. (30) are compared favorably with those obtained from eq. (1) as well as the Khan–Bhargava plot as shown in Table III. However, the present calculations are simpler than the two extrapolation procedures.

Equation (31) is more relevant to polystyrene in toluene at 30°C as it registers the smaller σ_k, based on the data collected by Sutterlin.[11] Here, the constants a, b, m, and n are assessed to be -0.234, 0.744, -1.0, and -0.10 respectively, for $[\eta]$ varying from 0.1 to 2.0 dL/g. Incidentally, Weissberg et al.[16] have also been interested in the above system. Table IV lists their results on $[\eta]$ and k produced by eq. (1) for the three distinct polystyrene samples. These precise data are compared with those based on the single-point measurements. Here the associated C gives the η_r that can be readily obtained by the conventional method using eq. (21) for large t at which the kinetic effect may be ignored. Clearly, eq. (32) is the most reliable one for the low and medium molecular weight resins. However, it is marginally less impressive than the other methods for the largest polystyrene displayed in Table IV. This is not unexpected as the calibrated m and n values are invalid for this particular application with $[\eta] > 2.0$ dL/g, indicating that the validity of eq.

TABLE IV
Comparison of $[\eta]$ (dL/g) Values Obtained by Various Methods for Three Polystyrene Samples in Toluene at 30°C[a] [16]

$\overline{M}_w$[b] $\times 10^{-5}$	0.58	1.46	6.00
$[\eta]$[c]	0.345 (0.514)[d]	0.689 (0.362)[d]	2.18 (0.273)[d]
C (g/dL)	1.170	0.880	0.365
η_r	1.49	1.76	1.95
$[\eta]$ [eq. (2)]	0.365	0.709	2.06
$[\eta]$ [eq. (3)]	0.380	0.753	2.22
$[\eta]$ [eq. (4)]	0.378	0.745	2.19
$[\eta]$ [eq. (5)][e]	0.377	0.740	2.14
$[\eta]$ [eq. (30)]	0.370 (0.302)[f]	0.646 (0.591)[f]	2.11 (0.300)[f]
$[\eta]$ [eq. (32)]	0.358 (0.408)[g]	0.699 (0.381)[g]	2.07 (0.342)[g]

[a] The system is characterized by $a = -0.234$, $b = 0.744$, $m = -1.0$, and $n = -0.1$.
[b] Weight-average molecular weight.
[c] Computed by eq. (1).
[d] Value of k computed by eq. (1).
[e] Assuming $[\eta] \gg 2.5/\rho$.
[f] Value of k computed by eq. (29).
[g] Value of k computed by eq. (31).

(31) is crucial in the present analysis. These findings are parallel to the comparisons of k values shown in Table IV, bearing in mind that the average k value of eqs. (2)–(5) is 0.28 as concluded earlier. It is believed that this calibrated method would be beneficial to the laboratories engaged in the routine $[\eta]$ determinations, which usually demand high degree of reliability, fast speed, and low cost.

CONCLUSIONS

The contemporary single-point estimation schemes for $[\eta]$ are confirmed to be inadequate in that they are only applicable to some specific polymer–solvent systems. Another existing simple $[\eta]$ method requires the service of a high performance viscometer. In this particular technique, an operative C that satisfies inequalities (17) and (18) must be predetermined. Alternatively, one may resort to a simplified version of the classical viscometry. This novel procedure hinges on either one of the two k–$[\eta]$ relationships established over the interested range of $[\eta]$, by either performing the viscometric experiments on a series of dilute polymer solutions covering a wide range of $[\eta]$ or by collecting the relevant information from the literature. For this purpose, the lengthy listing of $[\eta]$–k data for a variety of polymer–solvent combinations compiled by Sutterlin[11] would be most handy. Although, eqs. (30) and (32) are inherently inferior to the Huggins equation as for other one-parameter expressions cited, they are particularly useful for handling a larger number of $[\eta]$ determinations at a time, and for predicting $[\eta]$ rapidly in the event that the $[\eta]$ happens to be of secondary importance. In fact, the simple $[\eta]$ methods and the Huggins method are virtually playing two separate roles in characterizing the molecular weight of polymers. This means that the former practices are meant for fast or reasonably rough estimation of $[\eta]$, while the latter is best employed for procuring the accurate information on $[\eta]$. As such, they should not be applied irrationally. In that event, the practical significance of the proposed procedure is apparent. Obviously, the present analyses do not apply to the dilute polyelectrolyte solutions whose viscometric behavior is rather unique.

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