

On the Single-Point Determination of Intrinsic Viscosity

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Synopsis

In the present paper we have analytically derived a single-point equation for determining the intrinsic viscosity of a polymer. It is observed that the proposed equation gives a much better agreement with the extrapolated value of $[\eta]$ over a wide range of concentration for good as well as poor polymer-solvent systems.

INTRODUCTION

It is convenient to determine the intrinsic viscosity $[\eta]$ of a polymer by measurement of its viscosity in solution at a single concentration. Solomon and Ciuta¹ proposed the use of the following equation:

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

Narr et al.² have deduced this equation from the viscosity equation of Huggins³:

$$\frac{\eta_{sp}}{c} = [\eta] + K'[\eta]^2c \quad (2)$$

Solomon and Gotesman⁴ analytically derived another single-point equation

$$[\eta] = \frac{\eta_{sp}}{c} [1 + {}^{1/3}\eta_{sp}]^{-1} \quad (3)$$

The remarkably simple equations of Solomon and Ciuta and Solomon and Gotesman which contain no constant characteristic of polymer solvent system give fairly accurate values of $[\eta]$ at low concentrations. Shroff⁵ and Pechoc⁶ have shown that the Solomon-Ciuta equation is valid for good polymer solvent systems where K' of eq. (2) is $0.3 \leq K' \leq 0.4$. However, when K' is significantly out of this range, as is the case with poor solvents, these equations give $[\eta]$ values that differ considerably from the extrapolated value of $[\eta]$.

Deb and Chatterjee⁷ derived another single-point equation by eliminating K' from the Schulz-Blaschke⁸ equation:

$$\frac{\eta_{sp}}{c} = [\eta] + K'[\eta]\eta_{sp}. \quad (4)$$

Their equation is

$$[\eta] = \frac{1}{c} [3(\ln \eta_r - \eta_{sp} + 1/2\eta_{sp}^2)]^{1/3}. \quad (5)$$

The above equation was also derived by Palit and Kar⁹ by assuming $K' = 0$ and including higher-order terms in the polynomial expansion of $\ln \eta_r$.

In the present paper we have derived a single-point equation by using the empirical viscosity relation of Schramek.¹⁰ Our equation gives accurate results for good as well as poor polymer solvent systems.

THEORETICAL ANALYSIS

We start from the empirical viscosity relation of Schramek¹⁰:

$$\frac{\eta_{sp}}{c} = f(c) = [\eta] \left[1 + \frac{K'[\eta]c}{m} \right]^m. \quad (6)$$

This equation has two parameters, K' and m , and is quite general. In fact, it reduces to the Huggins equation when $m = 1$, to the Schulz-Blaschke equation and Martin¹⁰ equation when $m = -1$ and ∞ , respectively.

The function $\ln \eta_r/c$ is denoted by $\Phi(c)$. By the definition of intrinsic viscosity, we have

$$[\eta] = \lim_{c \rightarrow 0} \frac{\eta_{sp}}{c} = f(0) \quad (7)$$

$$[\eta] = \lim_{c \rightarrow 0} \frac{\ln \eta_r}{c} = \Phi(0)$$

Functions $f(c)$ and $\Phi(c)$ can be expanded in Taylor-Maclaurin form,

$$f(c) = f(0) + cf'(0) + \frac{c^2}{2!} f''(0) + \dots \quad (8)$$

$$\Phi(c) = \Phi(0) + c\Phi'(0) + \frac{c^2}{2!} \Phi''(0) + \dots \quad (9)$$

Since $\eta_r = 1 + \eta_{sp}$, $\ln \eta_r$ can be expanded in the following form (for $\eta_{sp} < 1$):

$$\ln \eta_r = \eta_{sp} - \frac{\eta_{sp}^2}{2} + \frac{\eta_{sp}^3}{3} - \dots \quad (10)$$

which gives

$$\Phi(c) = \frac{\ln \eta_r}{c} = \frac{\eta_{sp}}{c} - \frac{c}{2} \left(\frac{\eta_{sp}}{c} \right)^2 + \frac{c^2}{3} \left(\frac{\eta_{sp}}{c} \right)^3 - \dots \quad (11)$$

This can be written in the form

$$f(c) - \Phi(c) = \sum_{j=2}^{\infty} \frac{(-1)^j}{j} f^j(c) c^{j-1}. \quad (12)$$

From eqs. (8) and (9) we get

$$\eta_{sp} - \ln \eta_r = c[f(c) - \Phi(c)] = \sum_{n=0} \frac{f^{(n)}(0) - \Phi^{(n)}(0)}{n!} c^{n+1} \quad (13)$$

where $f^{(n)}(0)$ and $\Phi^{(n)}(0)$ denote the n th derivatives of f and Φ with respect to c at $c = 0$.

We shall now discuss various approximations of eqs. (12) and (13):

(a) It will be observed from eqs. (12) and (13) that $f(c) = \Phi(c)$ when $c = 0$, i.e., $f(0) = \Phi(0)$, which is the intrinsic viscosity by definition [eq. (7)]:

$$f(0) = \Phi(0) = [\eta].$$

(b) Differentiating eq. (13) with respect to c , we get

$$f'(c) - \Phi'(c) = \sum_{j=2} \frac{(-1)^j}{j} [(j-1)c^{j-2}f^j(c) + c^{j-1}\{f^j(c)\}']. \quad (14)$$

when $c = 0$,

$$f'(0) - \Phi'(0) = \frac{1}{2}f^2(0) = \frac{1}{2}[\eta]^2. \quad (15)$$

Substituting in eq. (13), we get

$$\eta_{sp} - \ln \eta_r = \frac{1}{2}[\eta]^2 c^2 \quad (16)$$

which is the Solomon-Ciuta equation.

(c) Terms higher than c^2 can be included in eq. (16) for a better approximation. This is achieved by including $f''(c) - \Phi''(c)$ in eq. (13). Differentiating eq. (14) with respect to c ,

$$f''(c) - \Phi''(c) = \sum_{j=2} \frac{(-1)^j}{j} [(j-1)(j-2)c^{j-3}f^j(c) + 2(j-1)c^{j-2}\{f^j(c)\}' + c^{j-1}\{f^j(c)\}'']. \quad (17)$$

Since $f'(0) = K'[\eta]^2$, from eq. (6), eq. (17) gives, for $c = 0$,

$$f''(0) - \Phi''(0) = 2(K' - \frac{1}{3})[\eta]^3. \quad (18)$$

Substituting eqs. (15) and (18) in eq. (13) gives

$$\eta_{sp} - \ln \eta_r = \frac{1}{2}[\eta]^2 c^2 + (K' - \frac{1}{3})[\eta]^3 c^3 \quad (19)$$

which can be reduced to the Solomon-Gotesman equation by eliminating K' from it with the help of the Huggins equation, eq. (2). For good polymer solvent systems, $K' \sim \frac{1}{3}$ and the second term on the right-hand side of eq. (19) is negligible in comparison with $\frac{1}{2}[\eta]^2 c^2$. Equation (19) thus reduces to the Solomon-Ciuta equation.

(d) For a better approximation, we included terms higher than $[\eta]^3 c^3$ in eq. (19). This is achieved by including $f'''(c) - \Phi'''(c)$ in eq. (13). Proceeding in the above manner, we get

$$f'''(0) - \Phi'''(0) = 3 \left[\frac{1}{2} - 2K' + \frac{2m-1}{m} K'^2 \right]. \quad (20)$$

Equation (13) gives

$$\eta_{sp} - \ln \eta_r = \frac{[\eta]^2 c^2}{2} \left[1 + 2 \left(K' - \frac{1}{3} \right) [\eta] c + \left(\frac{1}{2} - 2K' + \frac{2m-1}{m} K'^2 \right) [\eta]^2 c^2 \right]. \quad (21)$$

For $m = 1$, the above equation reduces to the modified single-point equation of Shroff.⁵

With the help of eq. (6), eq. (21) can be reduced to the following form:

$$[\eta] = \frac{1}{c} [2(\eta_{sp} - \ln \eta_r)]^{1/2} \left[1 - \left(K' - \frac{1}{3} \right) \eta_{sp} + \left\{ \left(\frac{3}{2} + \frac{1}{2m} \right) K'^2 - \frac{1}{3} \left(K' + \frac{1}{4} \right) \right\} \eta_{sp}^2 \right]. \quad (22)$$

For good polymer-solvent systems, $K' \simeq 1/3$, eq. (22) reduces to

$$[\eta] = \frac{1}{c} [2(\eta_{sp} - \ln \eta_r)]^{1/2} \left[1 + \left(\frac{1}{m} - \frac{1}{2} \right) \frac{\eta_{sp}^2}{18} \right]. \quad (23)$$

At low concentrations, $\eta_{sp}^2 \ll 1$, and our equation reduces to the Solomon-Ciuta equation. For higher concentrations or for the polymer-solvent systems where K' differs significantly from the value of $1/3$, the η_{sp} and η_{sp}^2 terms in eq. (22) give a significant contribution and hence cannot be neglected. Assuming $K' = 1/2$ for poor solvents, eq. (22) reduces to

$$[\eta] = \frac{1}{c} [2(\eta_{sp} - \ln \eta_r)]^{1/2} \left[1 - \frac{\eta_{sp}}{6} + \frac{\eta_{sp}^2}{8} \left(\frac{1}{m} - \frac{1}{2} \right) \right]. \quad (24)$$

DISCUSSION

Viscosity data on some polymer-solvent systems are taken from the literature. Intrinsic viscosity calculated with our equation is compared with that obtained from the Solomon-Ciuta, Solomon-Gotesman, and Deb-Chatterjee equations. The results for good and poor polymer-solvent systems are given in Tables I and II, respectively.

For good polymer-solvent systems, it is observed that the Solomon-Ciuta and Solomon-Gotesman equations give fairly accurate values of $[\eta]$ at low concentrations. At higher concentrations, however, the deviation from the extrapolated value of $[\eta]$ is considerable. This large error is due to neglect of higher-order terms in the derivation of these equations. However, the Solomon-Gotesman equation gives better results. The Deb-Chatterjee equation gives much higher values of $[\eta]$ even at low concentrations. This behavior of the Deb-Chatterjee equation is quite natural because in its derivation it was assumed that $K' = 0$. However, Gillespie and Hulme¹² have shown that the results obtained from this equation

TABLE I
Comparison of $[\eta]$ Values for Good Polymer-Solvent Systems

Polymer-solvent system	Concn., g/dl	$[\eta]$ Graph	$[\eta]$ Calculated				
			Solomon- Ciuta equation	Solomon- Gotesman equation	Deb- Chatterjee equation	Our equation $m = -1$ $m = 1$	
Poly(methyl methacrylate)- benzene ^a	0.15		1.260	1.252	1.266	1.258	1.261
	0.30	1.261	1.250	1.237	1.236	1.236	1.260
	0.45		1.244	1.216	1.228	1.228	1.260
Poly(vinyl acetate)- chloroform ^b	0.15		1.002	0.998	0.992	0.999	1.002
	0.30	1.000	0.998	0.991	1.023	0.992	1.002
Cellulose acetate- acetone ^c	0.45		0.994	0.981	1.038	0.989	1.002
	0.15		0.914	0.910	0.930	0.913	0.914
	0.30	0.920	0.934	0.926	0.945	0.928	0.935
Polystyrene-toluene ^d	0.45		0.958	0.944	0.975	0.933	0.953
	0.10		1.844	1.842	1.871	1.842	1.844
	0.15	1.843	1.857	1.844	1.890	1.843	1.860
0.20		1.866	1.843	1.919	1.845	1.879	

^a Data of Moore and Fort.¹³

^b Data of Daoust and Rinfret.¹⁴

^c Data of Phillip and Bjork.¹⁵

^d Data of Goldberg, Hohenstein, and Mark.¹⁶

TABLE II
Comparison of $[\eta]$ Values for Poor Polymer-Solvent Systems

Polymer-solvent system	Concn., g/dl	$[\eta]$ Graph	$[\eta]$ Calculated			
			Solomon- Ciuta equation	Gotes- man equation	Deb- Chatter- jee equation	Our equation $m = \infty$
Polyethylene- <i>p</i> - xylene ^a	0.15		0.980	0.950	1.003	0.957
	0.30	0.954	0.990	0.963	1.013	0.953
	0.45		1.003	0.980	1.036	0.950
Poly(methylmeth- acrylate)-acetone ^b	0.20		0.713	0.711	0.686	0.702
	0.40	0.694	0.728	0.722	0.740	0.700
	0.60		0.738	0.727	0.785	0.698
Poly(vinyl acetate)- acetophenone ^c	0.20		0.628	0.632	0.640	0.627
	0.40	0.621	0.642	0.640	0.642	0.623
	0.60		0.650	0.643	0.670	0.621
Polystyrene-15:85 acetone:methyl cyclohexane ^d	0.15		0.966	0.967	0.992	0.944
	0.30	0.945	0.989	0.981	1.003	0.948
	0.45		1.002	0.986	1.039	0.948

^a Data of Trementozzi.¹⁷

^b Data of Moore and Fort.¹³

^c Data of Daoust and Rinfret.¹⁴

^d Data of Palit, Colombo, and Mark.¹⁸

are identical with those obtained from the Huggins equation when $K' = 1/4$.

It is observed that our eq. (23) gives very good agreement with the extrapolated values of $[\eta]$. In extremely good polymer-solvent systems, our eq. (23) with $m = -1$ gives accurate results, whereas for fairly good polymer-solvent systems eq. (23) with $m = +1$ gives fairly accurate values of $[\eta]$. We can thus write our eq. (23) in the following form:

(i) For extremely good polymer-solvent systems:

$$[\eta] = \frac{1}{c} [2(\eta_{sp} - \ln \eta_r)]^{1/2} \left[1 - \frac{\eta_{sp}^2}{12} \right]. \quad (25)$$

(ii) For fairly good polymer-solvent systems:

$$[\eta] = \frac{1}{c} [2(\eta_{sp} - \ln \eta_r)]^{1/2} \left[1 + \frac{\eta_{sp}^2}{18} \right]. \quad (26)$$

For poor polymer-solvent systems, where $K' \sim 1/2$, the existing single-point equations give a very high value of

$$\Delta[\eta] = \frac{[\eta]_{\text{calc}} - [\eta]_{\text{expt}}}{[\eta]_{\text{expt}}} \times 100\%$$

at higher concentrations. Even here it is observed that the results obtained from the existing equations are in the following order:

$$[\eta]_{\text{Deb-Chatterjee}} > [\eta]_{\text{Solomon-Gotesman}} > [\eta]_{\text{Solomon-Ciuta}} > [\eta]_{\text{graph}}$$

Our eq. (24) for poor solvents with $m = \infty$ gives the best results. We can thus write the equation for poor polymer-solvent systems as

$$[\eta] = \frac{1}{c} [2(\eta_{sp} - \ln \eta_r)]^{1/2} \left[1 - \frac{\eta_{sp}}{6} - \frac{\eta_{sp}^2}{16} \right]. \quad (27)$$

For some polymer-solvent systems, however, it is observed that the value of K' is very much different from its value of $1/3$ and $1/2$ for good and poor systems, respectively. In such cases more accurate values of $[\eta]$ may be obtained by using the general eq. (22) if K' for that particular polymer-solvent system can be estimated.

CONCLUSIONS

It is concluded, therefore, that the existing single-point equations are valid only for good polymer-solvent systems, where $K' \sim 1/3$, at low concentrations. For poor polymer-solvent systems and also at higher concentrations, these equations give a poor agreement with the extrapolated value of $[\eta]$. Our eqs. (25) and (26) for good polymer-solvent systems and eq. (27) for poor polymer-solvent systems give a fairly accurate value of $[\eta]$ over a wide range of concentrations.

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