Determination of Intrinsic Viscosity from One Point Measurement

VLADIMÍR PECHOČ, *Research Institute of Chemical Fibres, Svit, Czechoslovakian S.R.*

Synopsis

The method of calculation of the intrinsic viscosity $[\eta]$ from one viscosity measurement according to the Solomon and Ciută's equation

$$[\eta]c = \sqrt{2} \sqrt{\eta_{sp} - \ln \eta_r}$$

has been analysed. The difference between $[\eta]$ extrapolated from the measurement of viscosity at several concentrations and $[\eta]$ calculated has been defined in dependence on the product $[\eta]c$ and the value of Huggins' constant k'. It has been demonstrated that the proposed equation is often useful but not generally valid; the range of its applicability has been defined.

1. Introduction

Solomon and Ciută recently reported a new equation for the determination of intrinsic viscosity from one viscosity measurement of the polymer solution.[1] Their equation,

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

contains no constant characteristic of polymer, solvent used, and temperature and ought to be quite general; this the authors have demonstrated in the quoted paper by comparing published data and their own of $[\eta]$ obtained by common extrapolation of the function $\eta_{sp}/c = f(c)$ and by calculation according to eq. (1). Though the data compared are in quite a good agreement it is not possible to agree without any restrictions with the proposed equation and with its postulated generality, as will be discussed below.

2. Theoretical Analysis of the Problem

There have been proposed many forms of the function $f(c)$ in the general equation $\eta_{sp}/c = f(c)$;[2-6] for small concentrations (up to ca. 1 g./100 ml.)* most of them can be transformed by series expansion and by neglecting higher powers of c into the form

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

* All concentrations are given in grams/100 ml. and intrinsic viscosity in 100 ml./g.

or

$$\ln \eta_r/c = [\eta] + k''[\eta]^2 c \qquad (3)$$

where k' and k'' are constant essentially independent of molecular weight, but characteristic of any polymer–solvent–temperature system.

Equation (2), known as Huggins' equation, is commonly used for calculation of intrinsic viscosity, if the value of k' is known. This constant can be deduced from a series of measurement of η_{sp} on polymer solutions at different concentrations. The plot of η_{sp}/c against c is linear, and the ratio of the slope of this straight line to the squared intercept at $c = 0$ (i.e., to the $[\eta]^2$) is k'.

Equations (2) and (3) give identical results. By series expansion of $\ln \eta_r$ we obtain

$$\ln \eta_r = \ln (\eta_{sp} + 1) = \eta_{sp} - \tfrac{1}{2}\eta_{sp}^2 + \tfrac{1}{3}\eta_{sp}^3 + \ldots \qquad (4)$$

For as c approaches zero, η_{sp} also approaches zero, and the series reduces then by retaining only the first term to

$$\ln \eta_r = \eta_{sp} \qquad (5)$$

so that

$$\lim_{c \to 0} \frac{\ln \eta_r}{c} = \lim_{c \to 0} \frac{\eta_{sp}}{c} \qquad (5a)$$

From this follows the relation between k' and k''. By subtracting eq. (3) from eq. (2) and rearranging we obtain

$$[\eta] = [1/c(k' - k'')^{1/2}](\eta_{sp} - \ln \eta_r)^{1/2} \qquad (6)$$

On substituting the series of eq. (4), eq. (6) becomes

$$[\eta] = [1/c(k' - k'')^{1/2}](\tfrac{1}{2}\eta_{sp}^2 - \tfrac{1}{3}\eta_{sp}^3 + \ldots)^{1/2} \qquad (7)$$

Comparing the definition of $[\eta]$, i.e., $[\eta] = \lim_{c \to 0} \eta_{sp}/c$, with the eq. (7), it follows for $c \to 0$ that

$$k' - k'' = 0.5 \qquad (8)$$

This relation is commonly known.[7,8] By its substitution eq. (6) is reduced to

$$[\eta]c = \sqrt{2}\sqrt{\eta_{sp} - \ln \eta_r} \qquad (9)$$

which is identical with Solomon and Ciută's eq. (1).

As evident from the analysis given above, eq. (1) is a combination of eqs. (2) and (3) and is valid only for $c \to 0$; for $c > 0$ the calculation error increases. The authors recommend the use of the value of η_{sp} determined at a concentration of $c = 0.2$ g./100 ml. It is silently presupposed that $c = 0.2$ g./100 ml. is above the critical concentration, where the function $\eta_{sp}/c = f(c)$ has its minimum. Nevertheless, the calculated value $[\eta]_{calc}$

is, even at these conditions, different from the value $[\eta]_{ex}$ obtained from eq. (2) that has a sound theoretical basis and has been amply verified experimentally. The difference between the calculated and extrapolated value of $[\eta]$ depends partly on the product $[\eta]c$, partly on the value of the constant k' according to equation

$$\Delta[\eta] = a + bk' \qquad (10)$$

where

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

and the constants a and b depend on the product $[\eta]c$ according to Table I or Figure 1.

TABLE I
Values of Constants a and b for Various $[\eta]c$

$[\eta]c$	$-a$	b
0.1	3.158	9.391
0.4	10.77	31.25
0.6	14.66	41.57
1.0	20.83	57.75
1.5	25.67	68.10
2.0	30.60	80.00

Equation (10) is sufficiently exact up to $[\eta]c = 2$; for higher values it has not been checked.

It follows from eq. (10) that the difference $\Delta[\eta]$ is zero for any $[\eta]c$, when k' is within the range $0.34 \leqslant k' \leqslant 0.38$; the exact value of k' at which the $\Delta[\eta]$ is zero, depends slightly on the value of $[\eta]c$. For smaller k' the difference is negative, for larger ones it is positive and increases in both cases in absolute value with $[\eta]c$. Equation (10) gives also quite generally the dependence of the difference $\Delta[\eta]$ on the concentration of solution used in the measurement of η_{sp}.

3. Comparison of Theoretical Analysis with Experimental Data

The authors checked their equation by comparing $[\eta]_{calc}$ with various values of $[\eta]_{ex}$ published in the scientific literature. For the sake of brevity we shall limit our calculations only to the calculation of intrinsic viscosity of polyethylene in p-xylene data of Trementozzi,[9] which will be most objective for the appreciation of applicability and fitness of the proposed eq. (1).

The authors chose for comparison the sample A-8[9] with intrinsic viscosity $[\eta] = 0.54$ and $k' = 0.27$. According to eq. (10) and Figure 1 it can be calculated that the difference $\Delta[\eta]$, using η_{sp} measured at the con-
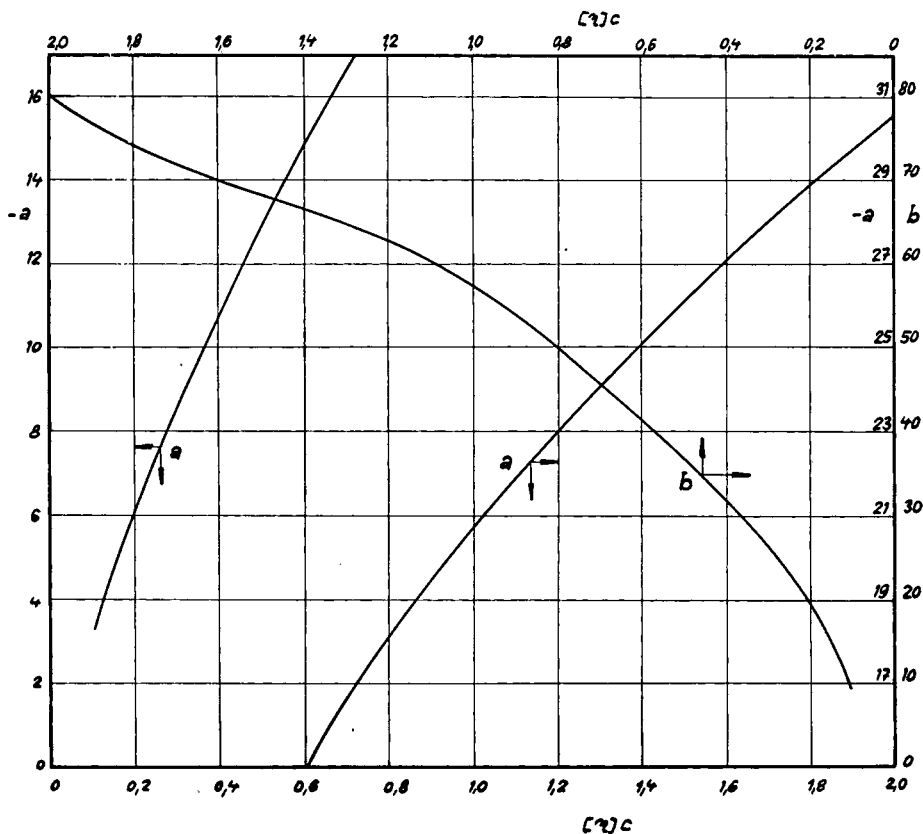
Fig. 1. The plot of the constants a and b of eq. (10) against $[\eta]c$.   (See Table I.)

centration $c = 0.2$ g./100 ml. will be -0.7%, with η_{sp} at $c = 0.88$, $\Delta[\eta] = -2.7\%$.   By substituting η_{sp} calculated from the equation

$$\eta_{sp} = 0.54c(1 + 0.27 \times 0.54c)$$

into eq. (1), we have, for $c = 0.2$:

$$\eta_{sp} = 0.1111$$

$$[\eta]_{calc} = 0.536$$

$$\Delta[\eta] \doteq -0.7\%$$

and for $c = 0.88$:

$$\eta_{sp} = 0.5362$$

$$[\eta]_{calc} = 0.525$$

$$\Delta[\eta] \doteq -2.8\%$$

In this case it is evident that the exact calculation by eq. (1) gives even better results than have been given by the authors in Tables I and II of their paper, and that the accuracy is only slightly influenced by the concentration used. The reason for this is in the first place the small value of $[\eta]c$ and then the fact that the value of k' is rather near the value at which $\Delta[\eta] = 0$ for any $[\eta]c$.

The agreement of $[\eta]_{calc}$ and $[\eta]_{ex}$, however, is not so good with other samples. Sample B-3,[9] for example, has $[\eta] = 1.75$ and $k' = 1.06$. At the concentration $c = 0.2$ the product $[\eta]c = 0.35$. The constants a and b of eq. (10) are $a = -9.6$, $b = 28.0$ (see Fig. 1), and the difference according to eq. (10) is:

$$\Delta[\eta] = -9.6 + 28.0 \times 1.06 = 20\%$$

Calculating $[\eta]_{calc}$ by substitution of $\eta_{sp} = 0.48$ at $c = 0.2$ into eq. (1) we get

$$[\eta]_{calc} = 2.10$$

so that actually

$$\Delta[\eta] = \frac{2.10 - 1.75}{1.75} = 20\%.$$

The great difference is caused by a high value of k'.

The difference of calculated and extrapolated values in this example is due to the dependence of k' on molecular weight of various fractions of polyethylene; this is therefore an extraordinary case, as the constant k' is usually independent on molecular weight. It depends, however, on the solvent and temperature used; for the solutions of polystyrene in toluene, for example, its value at 30°C. is $k' = 0.37$, whereas for solutions of the same polymer in cyclohexane at the same temperature $k' = 0.74$.[10a] The value of k' for polystyrene in toluene varies further from 0.21 to 0.42 with the temperature at which the polystyrene was polymerized.[10b] For $k' = 0.37$, the results of calculation are sufficiently exact; for $k' = 0.74$ the difference $\Delta[\eta]$ at $[\eta]c = 0.6$ is $\Delta[\eta] \doteq 16\%$, for $k' = 0.21$ at the same $[\eta]c$ the difference is $\Delta[\eta] = -5.9\%$.

The supposed general applicability of eq. (1) is very unfavorably influenced by all these facts.

4. Conclusion

It is evident that it is impossible to regard eq. (1) as a generally valid equation for the determination of $[\eta]$ from one point measurement. It is applicable only when the constant k' of eq. (2) is $0.30 \leqslant k' \leqslant 0.45$. Even in this range of k', the difference $\Delta[\eta]$ between the calculated and extrapolated values of $[\eta]$ depends on the value of $[\eta]c$, but for the limiting value $[\eta]c = 2$ it is within the interval $\Delta[\eta] = -6$ to $+5.6\%$. For smaller $[\eta]c$ and for k' between the given extreme values the difference becomes smaller. For k' outside this interval, however, the difference substan-

tially increases with increasing $[\eta]c$; it may be quite a large one, even for not too high values of $[\eta]c$.

For reliable application of eq. (1) it is consequently necessary to know at least approximately the value of the Huggins' constant k' for the given polymer–solvent system for the given temperature and range of molecular weight. Although many polymer solutions have at normal conditions a suitable value of k', eq. (1) must nevertheless be characterized only as a good tool to facilitate the work in numerous serial analyses of the system for which its validity was checked in advance. Thus it represents an equation of the same type as the equation published earlier by Maron[11] without any pretense to general validity.

References

1. Solomon and Ciutǎ, *J. Appl. Polymer Sci.*, **6**, 683 (1962).

2. Baker, F., *J. Chem. Soc.*, **103**, 1653 (1913).

3. Kraemer, E. O., *Ind. Eng. Chem.*, **30**, 1200 (1938).

4. Schulz, G. V., and F. Blaschke, *J. Prakt. Chem.*, **158**, 130 (1941).

5. Huggins, M. L., *J. Am. Chem. Soc.*, **64**, 2716 (1942).

6. Martin, A. F., after E. Ott and H. M. Spurlin, *Cellulose and Cellulose Derivatives*, Vol. III, 2nd Ed., Interscience, New York–London, 1955, p. 1189.

7. Huggins, M. L., *Ind. Eng. Chem.*, **35**, 980 (1943).

8. Immergut, E. H., and F. R. Eirich, *Ind. Eng. Chem.*, **45**, 2500 (1953).

9. Trementozzi, Q. A., *J. Polymer Sci.*, **23**, 887 (1957).

10. (a) Ewart, R. H., after R. H. Boundy and R. F. Boyer, *Styrene, its Polymers, Copolymers and Derivatives*, Reinhold, New York, 1952, p. 332. (b) T. Alfrey, A. Bartovics, and H. Mark, *ibid.*

11. Maron, S. H., *J. Appl. Polymer Sci.*, **5**, 282 (1661).

Résumé

On a analysé la méthode de calcul de la viscosité intrinsèque $[\eta]$ à partir d'une mesure de viscosité d'après l'équation de Solomon et Ciutǎ:

$$[\eta]c = \sqrt{2}\,\sqrt{\eta_{sp} - \ln \eta_r}$$

La différence entre $[\eta]$ extrapolée à partir de mesures de viscosité à plusieurs concentrations et $[\eta]$ calculée a été définie en fonction du produit $[\eta]c$ et de la valeur de la constante k' de Huggins. On a demontré que l'équation proposée est souvent utile mais pas généralement valide; on a défini son domaine d'application.

Zusammenfassung

Die Berechnung der Viskositätszahl $[\eta]$ aus einer Viskositätsmessung nach der Gleichung von Solomon und Ciutǎ

$$[\eta]c = \sqrt{2}\,\sqrt{\eta_{sp} - \ln \eta_r}$$

wurde einer Analyse unterzogen. Der Unterschied zwischen dem aus Viskotitätsmessungen bei verschiedenen Konzentrationen extrapolierten Wert und dem berechneten Wert von $[\eta]$ wurde in Abhängigkeit vom Produkt $[\eta]c$ und dem Wert der Huggins-Konstante k' dargestellt. Es wurde gezeigt, dass die vorgeschlagene Gleichung zwar oft brauchbar, aber nicht allgemein gültig ist; ihr Anwendungsbereich wurde festgelegt.