Determination of Intrinsic Viscosity from One-Point Measurements

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INTRODUCTION

Many laboratories have occasion to determine the intrinsic viscosities of samples of the same polymer at different molecular weights. These operations, if performed properly, are very tedious and time-consuming, since the viscosity of each sample has to be measured at at least three different solution concentrations. To obviate these difficulties measurements are frequently made at one dilute concentration, and the η_{sp}/C value, where η_{sp} is the specific viscosity and C the concentration, is considered to be the intrinsic viscosity, $[\eta]$. However, such determinations are only approximations, and a method is desired which would yield $[\eta]$ and not η_{sp}/C from the viscosity. Such a method is described in the present paper.

Mathematical Considerations

Intrinsic viscosities are generally determined by plotting either η_{sp}/C or $\ln \eta_r/C$, where η_r = relative viscosity, against C, and extrapolating to $C = 0$. In the region of linearity the plots obtained have the appearance of the curves shown in Figure 1. The equations of these lines can be written as

$$\eta_{sp}/C = [\eta] + \alpha C \qquad (1)$$

$$\ln \eta_r/C = [\eta] - \beta C \qquad (2)$$

where α and β are constants. Let now

$$\gamma = \alpha/\beta \qquad (3)$$

If we now multiply eq. (2) by γ, the result is

$$(\gamma \ln \eta_r)/C = \gamma [\eta] - \alpha C \qquad (4)$$

Adding now eqs. (1) and (4), we get

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

and therefore

$$[\eta] = \frac{(\eta_{sp}/C) + [\gamma(\ln \eta_r)/C]}{(1 - \gamma)}$$

$$= \frac{\eta_{sp} + \gamma \ln \eta_r}{(1 + \gamma)C} \qquad (5)$$

It is a well known fact that the constants α and β are related to the intrinsic viscosity by the equations

$$\alpha = k_1[\eta]^2 \qquad (6)$$

$$\beta = k_1'[\eta]^2 \qquad (7)$$

where k_1 and k_1' are constants independent of molecular weight. From eqs. (6) and (7), γ follows as

$$\gamma = \alpha/\beta = k_1/k_1' \qquad (8)$$

and hence for each polymer–solvent system at a given temperature γ should be a constant independent of the molecular weight. Therefore, if γ were determined on *one* sample of a polymer in a given solvent, the same value of γ should apply to all other samples, and eq. (5) should be sufficient to yield $[\eta]$ from a single viscosity measurement.
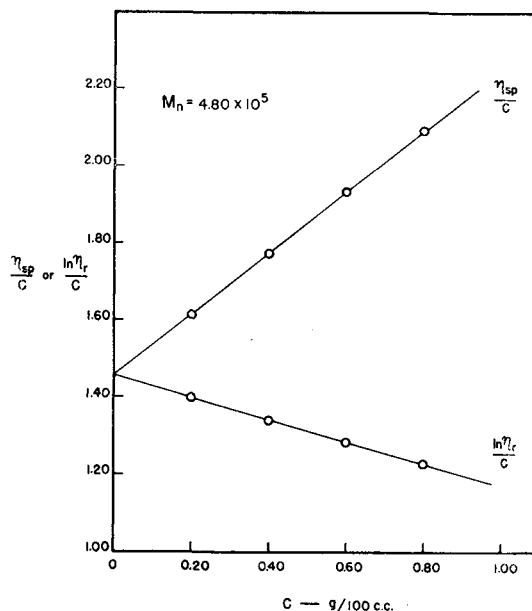

Fig. 1. Plot of η_{sp}/C and $\ln \eta_r/C$ for a sample of poly styrene in toluene at 30°C.

TABLE I
Comparison of Calculated and Observed Intrinsic Viscosities

Sample	M_n	C, g./100 cc.	$\frac{\eta_{sp}}{C}$	$\frac{\ln \eta_r}{C}$	$[\eta]$ Calc.	$[\eta]$ Obs.
Polystyrene in Toluene at 30°C.;[1] $\gamma = 2.73$
f	2.04×10^5	0.20	0.781	0.725	0.74	0.73
	"	0.40	0.831	0.718	0.75	"
	"	0.60	0.882	0.708	0.75	"
	"	0.80	0.932	0.696	0.76	"
d	9.06×10^5	0.20	2.100	1.754	1.85	1.85
	"	0.40	2.351	1.657	1.84	"
	"	0.60	2.603	1.568	1.85	"
	"	0.80	2.854	1.486	1.85	"
b	1.41×10^6	0.20	2.778	2.210	2.36	2.34
	"	0.40	3.212	2.066	2.36	"
	"	0.60	3.646	1.933	2.39	"
	"	0.80	4.080	1.813	2.42	"
a	1.81×10^6	0.20	4.006	2.943	3.23	3.23
	"	0.40	4.782	2.673	3.23	"
	"	0.60	5.558	2.445	3.27	"
	"	0.80	6.334	2.254	3.35	"
Cellulose Acetate in Acetone at 25°C.;[2] $\gamma = 5.33$
14	2.4×10^4	0.147	0.610	0.573	0.578	0.59
	"	0.335	0.630	0.569	0.578	"
	"	0.587	0.660	0.561	0.578	"
11	4.2×10^4	0.149	1.20	1.11	1.13	1.13
	"	0.297	1.30	1.10	1.13	"
	"	0.625	1.50	1.06	1.13	"
8	6.1×10^4	0.138	1.74	1.55	1.58	1.60
	"	0.275	1.89	1.53	1.59	"
	"	0.428	2.07	1.48	1.57	"
4	8.6×10^4	0.114	2.52	2.21	2.26	2.25
	"	0.351	3.13	2.11	2.27	"
	"	0.703	4.43	2.01	2.18	"
2	13.0×10^4	0.094	3.08	2.70	2.76	2.75
	"	0.273	3.66	2.54	2.72	"
	"	0.546	5.08	2.43	2.85	"
Unfractionated	4.2×10^4	0.126	1.73	1.56	1.59	1.59
	"	0.268	1.87	1.51	1.57	"
	"	0.537	2.25	1.48	1.60	"

Test Of Equation (5)

The parameter γ is obtained readily from a plot such as Figure 1 simply by taking the two slopes and then getting their ratio. Once this parameter is available, single point calculations can be made from viscosity measurements by means of eq. (5).

In Table I are given some single point $[\eta]$'s calculated in this manner for polystyrene in toluene at 30°C.,[1] and for cellulose acetate in acetone at 25°C.[2] For the first of these systems γ was found to be 2.73, while for the second 5.33.

From this table it can be seen that the agreement among the individual values of $[\eta]$ for a given

sample is very good, as is also the agreement between the calculated values of $[\eta]$ and those observed by plotting η_{sp}/C vs. C and extrapolating to $C = 0$.

References

1. Goldberg, A. I., W. P. Hohenstein, and H. Mark, *J. Polymer Sci.*, **2**, 503 (1947).
2. Sookne, A. M., and M. Harris, *Ind. Eng. Chem.*, **37**, 475 (1945).

Synopsis

A method is described by means of which reliable intrinsic viscosities, $[\eta]$, can be obtained for a polymer–solvent system from viscosities determined at only one concentration. The

method involves, first, the preparation for one sample of the polymer of an η_{sp}/C and ln η_r/C vs. C plot. The ratio of the slopes of these two curves yields then a parameter γ which is independent of molecular weight, and which allows single point $[\eta]$ determinations on samples of the polymer at any other molecular weight, whether homogeneous or not. Results are presented to show that the method described yields $[\eta]$'s in good agreement with those obtained in the usual manner from multipoint viscosity measurements.

Résumé

Une méthode est décrite permettant de déterminer des viscosités intrinsèques dignes de confiance au départ de mesures de viscosités à une seule concentration pour un système polymère–solvant déterminé. D'abord, la méthode contient la préparation d'un diagramme de η_{sp}/C et ln η_r/C par rapport à C pour un seul échantillon du polymère. Le rapport des pentes de ces deux courbes donne alors un paramètre γ, qui est indépendant du poids moléculaire et qui permet des déterminations $[\eta]$ aux dépens de points uniques avec des échantillons du polymère de n'importe quel autre poids moléculaire, qu'il soit homogène ou non.

Zusammenfassung

Eine Methode zur Ermittlung verlässlicher Viskositätszahlen, $[\eta]$, für ein Polymer-Lösungsmittelsystem aus der Messung der Viskosität bei einer einzigen Konzentration wird beschrieben. Es muss zuerst für eine Probe des Polymeren ein η_{sp}/C und ein ln η_r/C-gegen-C Diagramm angefertigt werden. Das Verhältnis der Neigung dieser beiden Kurven ergibt einen Parameter γ, welcher vom Molekulargewicht unabhängig ist und eine Einpunkt-Bestimmung von $[\eta]$ an Polymerproben mit beliebigem Molekulargewicht, gleichgültig homogen oder nicht, erlaubt