

## Single-Point Determination of Intrinsic Viscosity

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Conventional procedures for the determination of intrinsic viscosity require measurement of specific viscosity at several concentrations followed by extrapolation to infinite dilution. When less precision is required, calculation of the intrinsic viscosity from a single measurement is an attractive possibility.<sup>1-3</sup>

Hart<sup>1</sup> rearranged the equation of Schulz and Blaschke<sup>4</sup> in the form:

$$[\eta] = (\eta_{sp}/c) N / (\eta_{sp} + N) \quad (1)$$

where  $N$  is the reciprocal of  $k$  in the Schulz-Blaschke equation. Hart used a graphical relation between  $N$  and specific viscosity in estimating  $[\eta]$  from a single measured viscosity.

In determining the intrinsic viscosities of stereoregular polybutene-1 samples in Decalin it was found that intrinsic viscosities could be estimated

TABLE I  
Comparison of Observed and Calculated Intrinsic Viscosities for Polybutene-1 Samples in Decalin at 115°C. for  $N = 2.08$

Sample	[ $\eta$ ]	
	Calculated by eq. (1)	Extrapolated
Pentane-Soluble Polymer		
Unfractionated	0.97	0.98
F-1	1.82	1.80
F-2	0.92	0.92
F-3	0.61	0.60
F-4	0.45	0.45
F-5	0.29	0.30
F-6	0.23	0.23
F-7	0.19	0.18
Pentane-Insoluble Polymer		
Unfractionated	3.23	3.15
F-1	2.35	2.34
F-1a	1.81	1.80
F-3	1.91	1.89
F-4	1.31	1.34
F-6	0.79	0.78

with reasonable precision for both the unfractionated material and the fractions obtained from it by using eq. (1) with  $N = 2.08$ , provided the measured

TABLE II  
 $N$  Values for Various Polymer-Solvent Systems

Polymer	Solvent	Temperature, °C.	$N$
Poly(methyl methacrylate)	Methyl ethyl ketone	25	2.00
Poly(methyl methacrylate)	Acetone	25	2.00
Poly(methyl methacrylate)	Toluene	25	3.07
Poly(methyl methacrylate)	CCS <sup>a</sup>	23	2.00
Poly(ethyl methacrylate)	Methyl ethyl ketone	23	3.00
Poly(ethyl methacrylate)	CCS <sup>b</sup>	23	1.20
Poly( <i>n</i> -butyl methacrylate)	Methyl ethyl ketone	23	2.79
Poly( <i>n</i> -butyl methacrylate)	Isopropanol <sup>c</sup>	21.5	1.00
Poly(2-ethylbutyl methacrylate)	Methyl ethyl ketone	25	3.30
Poly(2-ethylbutyl methacrylate)	Isopropanol <sup>c</sup>	27.4	1.12
Poly( <i>n</i> -hexyl methacrylate)	Methyl ethyl ketone	23	2.75
Poly( <i>n</i> -hexyl methacrylate)	Isopropanol <sup>c</sup>	32.6	1.42
Poly( <i>n</i> -octyl methacrylate)	Methyl ethyl ketone	23	2.17
Poly( <i>n</i> -octyl methacrylate)	<i>n</i> -Butanol <sup>c</sup>	16.8	1.25
Poly( <i>n</i> -lauryl methacrylate)	<i>n</i> -Butyl acetate	23	2.61
Poly( <i>n</i> -lauryl methacrylate)	Isopropyl acetate <sup>c</sup>	13	1.70

<sup>a</sup> Critical consolute solvent: methyl ethyl ketone-isopropanol, 55:45 by volume.

<sup>b</sup> Critical consolute solvent: methyl ethyl ketone-isopropanol, 1:7 by volume.

<sup>c</sup>  $\Theta$  solvent.

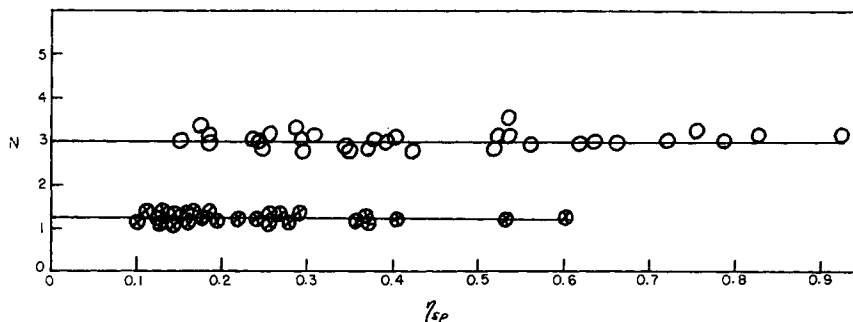


Fig. 1.  $N$  vs.  $\eta_{sp}$  for poly(ethyl methacrylate) (O) in methyl ethyl ketone and (⊗) in a critical consolute solvent.

$\eta_{sp}$  did not exceed approximately 1. A comparison of the intrinsic viscosities determined in the usual way with those calculated from a single point by eq. (1) is shown in Table I.

The polybutene-1 samples were obtained from the Sun Oil Co. and included pentane-soluble and also pentane-insoluble material. X-ray patterns showed both samples to be highly crystalline. Each was fractionated at 115°C. from cyclohexanone-Decalin (6:5 by volume), cyclohexanol-glycol (3:1 by volume) being used as the non-solvent. Intrinsic viscosity measurements were made in Decalin at 115°C. in an Ubbelohde viscometer.

The same single-point method was applied to a series of alkyl methacrylate polymer fractions previously studied.<sup>5-10</sup> In both good and poor solvents a single value of  $N$  was sufficient to calculate the intrinsic viscosity from a single specific

viscosity if the  $\eta_{sp}$  value was below 1.  $N$  values in all cases were obtained by using complete viscosity data for at least three fractions.

$N$  values that were found to be satisfactory for these systems are given in Table II. Typical results comparing single-point calculated and observed intrinsic viscosities for poly(ethyl methacrylate) in a good and in a poor solvent are shown in Table III. The constancy for  $\eta_{sp}$  with  $N$  for values below 1 is illustrated for these same systems in Figure 1. Figure 2 shows the variation of  $N$  with  $\eta_{sp}$  at higher specific viscosities.

Using a single  $N$  value for each of the systems studied, we found that if care was taken in measuring the single viscosity at a concentration low enough to give a specific viscosity value somewhat below 1, intrinsic viscosities could generally be calculated which fell within the experimental error of the complete extrapolation procedure.

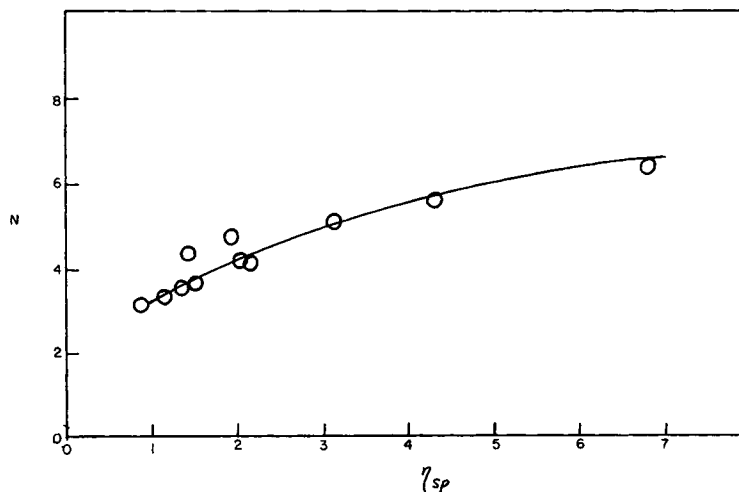


Fig. 2.  $N$  vs.  $\eta_{sp}$  for poly(ethyl methacrylate) in methyl ethyl ketone.

TABLE III

Comparison of Observed and Calculated Intrinsic Viscosities for Poly(ethyl Methacrylate) Fractions in Methyl Ethyl Ketone at 23°C. and in a Critical Consolute Solvent (Methyl Ethyl Ketone: Isopropanol; 1:7 by Volume) at 23°C.

Fraction	[ $\eta$ ]	
	Calculated by eq. (1)	Extrapolated
In Methyl Ethyl Ketone		
F-2	2.48	2.51
F-3	2.27	2.32
F-4	1.92	1.90
F-5	1.46	1.47
F-6	1.13	1.13
F-7	0.97	0.97
F-8	0.78	0.77
F-9	0.60	0.61
F-10	0.42	0.42
In Critical Consolute Solvent		
F-2	0.63	0.63
F-3	0.60	0.60
F-4	0.58	0.57
F-5	0.45	0.45
F-6	0.36	0.37
F-7	0.35	0.35
F-8	0.30	0.30
F-9	0.26	0.26
F-10	0.22	0.22

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### Synopsis

The Schulz and Blaschke equation in the rearranged form of Hart was used for reasonably precise calculation of the intrinsic viscosity from a single measured specific viscosity for stereoregular polybutene-1 in Decalin and for a series of alkyl methacrylate polymers in good and poor solvents. A single value of  $N$  can be used for each system provided careful measurements are made at specific viscosities somewhat below 1.

### Résumé

L'équation de Schulz et Blaschke, sous la forme réarrangée de Hart a été utilisée pour des calculs de viscosité intrinsèque d'une précision raisonnable à partir d'une simple mesure de viscosité spécifique effectuée sur de polybutene-1 stéréorégulier dans la décaline et sur une série de polyméthacrylate d'alcyle dans des solvants bons et mauvais. Une valeur unique de  $N$  peut être utilisée pour chaque système pourvu qu'on ait fait des mesures soigneuses à des viscosités spécifiques quelque peu inférieures à 1.

### Zusammenfassung

Die Gleichung von Schulz und Blaschke in der von Hart modifizierten Form wurde zu einer annehmbar genauen Berechnung der Viskositätszahl aus einem Messwert der spezifischen Viskosität für stereospezifisches Polybuten-1 in Dekalin und für eine Reihe von Alkylmethacrylatpolymeren in guten und schlechten Lösungsmitteln verwendet. Ein einziger  $N$ -Wert kann für jedes System benutzt werden, vorausgesetzt dass sorgfältige Messungen bei einer spezifischen Viskosität etwas unterhalb 1 durchgeführt werden.

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