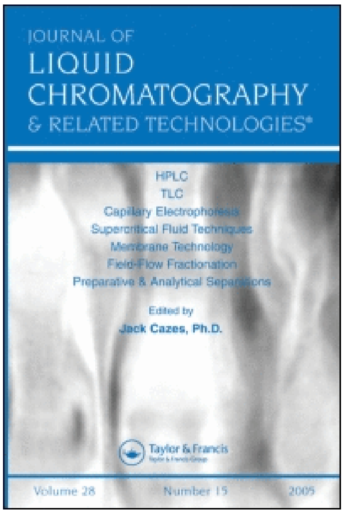

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CALCULATION OF INTRINSIC VISCOSITY FROM SIZE EXCLUSION CHROMATOGRAPHY DATA. THE INFLUENCE OF CONCENTRATION.

By

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Increasing use of data processors to manipulate the size exclusion chromatography data makes it possible to calculate intrinsic viscosity without any additional experimental work. In thermodynamically good solvents, which are most generally used for size exclusion chromatography work, the concentration effect is not negligible. Effect of this parameter on the calculation of intrinsic viscosity is shown.

INTRODUCTION

The viscosity average molecular weight ($\bar{M}_v$) can be calculated from the size exclusion chromatography (SEC) data using,

$$\bar{M}_v = \left[\frac{\sum_{i=1}^{N} Hi\,(Mi)^a}{\sum Hi}\right]^{1/a} \qquad (1)$$

where Hi is the height of the chromatogram at equally spaced intervals along the retention volume axis; Mi, molecular weight of species eluting from the column at points where Hi values are taken; and a, the Mark-Houwink exponent. Using the $\bar{M}_v$ one can calculate intrinsic viscosity [η] using the familiar Mark-Houwink relationship,

$$[\eta] = K\bar{M}_v^{a} \text{ or } \bar{M}_v[\eta] = K\bar{M}^{a+1} \tag{2}$$

where the constants K and *a* are usually determined using narrow dispersity standards. Equations (1) and (2) can be used to calculate $[\eta]$, the intrinsic viscosity of an unknown sample as it is fractionated into a series of narrowly dispersed fractions by the SEC process. The advantage of this technique first pointed out by Cazes (1) and Hellman (2) is convenience. Once the polymer solution is injected to the SEC columns, no further experimental work is necessary. It is even more convenient with Waters 730 Data Module which not only provides values for the size exclusion chromatogram (e.g., number average, weight average, Z-average and viscosity average) but simultaneously provides the intrinsic viscosity value, provided proper Mark-Houwink constants are inserted in the program. Results are presented here on the influence of concentration on the calculation of such data for polystyrene and the random copolymer styrene-n-butylmethacrylate (65/35).

EXPERIMENTAL

Narrow dispersity polystyrenes (MWD$\approx$1.1) were obtained from Pressure Chemical Company, Pittsburgh, Pa. Styrene-n-butylmethacrylate random copolymers (65/35) were prepared by suspension polymerization. The weight average molecular weights ranged from 24,500 to 224,600 with an average dispersity of 2.5 as determined by size exclusion chromatography and light scattering measurements. Intrinsic viscosities were measured in Cannon-Ubbelohde type capillary viscometers at 25^{o}C in chloroform (Burdick and Jackson, Muskegon, Michigan). The viscometer constants ranged from 0.001180 to 0.0383. Measurements were made in a thermostatically controlled bath maintained at 25°±0.01°C. All solvents and solutions were filtered before use. The intrinsic viscosity was calculated from reduced viscosity by means of Huggins relationship (3).

$$\eta_{sp}/C = [\eta] + K_1[\eta]^2C$$

Waters 150C ALC/GPC was used with 2X linear μ-Bondagel columns along with Waters 730 Data Module. Chloroform was used as solvent at room temperature. Area slices were integrated from just before the emergence of the peak to slightly after the peak when the baseline had attained its original value.

RESULTS AND DISCUSSION

The Mark-Houwink relationship obtained from the viscosity data are as follows:

$[\eta] = 7.6 \times 10^{-4}\bar{M}_V^{0.71}$ for polystyrene

and $[\eta] = 2.27 \times 10^{-4}\bar{M}_V^{0.65}$ for styrene n-butylmethacrylate (65/35)

Results of intrinsic viscosity data obtained from SEC and those from calculations via the Mark-Houwink relationship are presented in Table 1. It is obvious that as the injection volume is increased, the [η] obtained via the SEC decreases. This effect is shown graphically in Figure 1. The dependence of elution volume (Ve) and the width of the elution curve (w) on concentration (g) and volume of polymer solution injected has been observed by many workers (4-9). The concentration effect complicates the determination of polymer molecular weights, its distribution function and consequently the calculation of [η] from these data. Originally the reason for the concentration phenomenon was attributed to the viscosity effects in the system (4) and was called 'viscous fingering.' It was reasoned that with an increase in the viscosity of the sample, Comparison of Intrinsic Viscosities in Chloroform at 25°C Obtained by SEC and Viscometric Methods

Polymer	$\bar{M}_w$	$[\eta]$ Viscometric (1)	Injection Volume μl*	$[\eta]$ SEC (2)	% Difference (1-2)
Polystyrene	4,000	0.258	10	0.232	-10.0
			25	0.223	-13.0
			50	0.221	-14.3
			100	0.208	-19.3
	20,500	0.825	10	0.855	+ 3.6
			25	0.834	+ 1.1
			50	0.809	- 1.9
			100	0.769	- 6.8
	50,000	1.56	10	1.54	- 1.3
			25	1.50	- 3.8
			50	1.43	- 8.3
			100	1.34	-14.1
	110,000	2.72	10	2.95	+ 8.4
			25	2.78	+ 2.2
			50	2.62	- 3.7
			100	2.38	-12.5
	233,000	4.36	10	5.50	+26.1
			25	5.04	+15.1
			50	4.62	+ 6.0
			100	4.13	- 5.3
	600,000	9.06	10	10.6	+17.0
			25	9.34	+ 3.1
			50	8.27	- 8.7
			100	7.17	-20.1

Table 1 (cont'd)

Polymer	$\bar{M}w$	[η] Viscometric (1)	Injection Volume μl*	[η]SEC (2)	% Difference (1-2)
styrene-n-butyl methacrylate copolymer (65/35)	24,500	0.161	10	0.163	+ 1.2
			25	0.162	+ 0.6
			50	0.147	- 8.7
			100	0.144	-10.5
	66,000	0.298	10	0.325	+ 9.1
			25	0.305	+ 2.3
			50	0.260	-12.7
			100	0.250	-16.1
	95,200	0.440	10	0.462	+ 5.0
			25	0.454	+ 3.2
			50	0.442	+ 0.4
			100	0.437	- 0.7
	132,000	0.502	10	0.486	- 3.2
			25	0.471	- 6.2
			50	0.463	- 7.8
			100	0.458	- 8.8
	244,600	0.713	10	0.681	- 4.5
			25	0.672	- 5.7
			50	0.665	- 6.7
			100	0.655	- 8.1

*0.33% weight/volume concentration

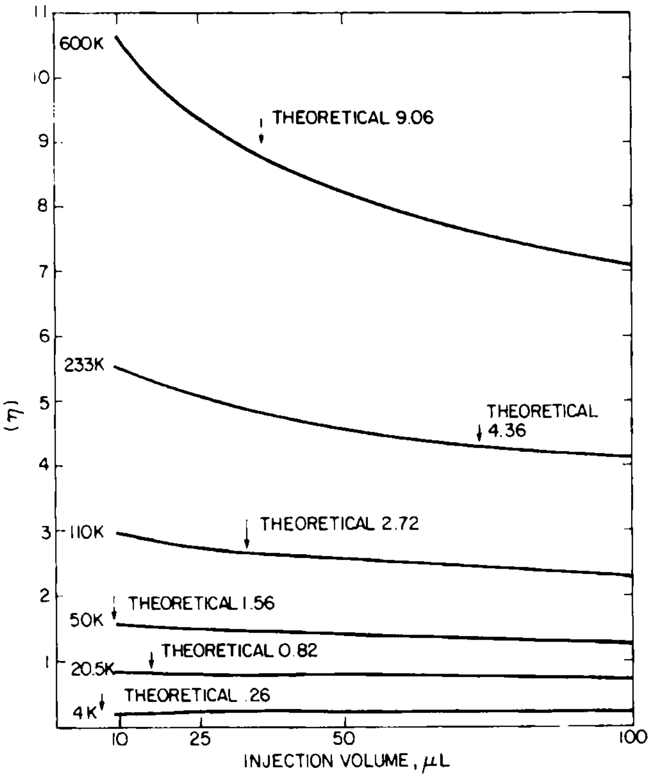

Figure 1. Variation of Intrinsic Viscosity of Polystyrenes with Injection Volume.

the mobile phase creates 'fingers' as it passes through the column resulting in a distorted peak and/or an increased Ve. It was also suggested that the decrease in hydrodynamic volume, as a result of macromolecular crowding manifests itself in an increase in Ve. Boni and coworkers (5,6) observed that the change, dVe/dg, was a linear function of log molecular weight. Also, if a polydisperse sample contains a significant amount of excluded polymer, the activity of permeable molecules in the interstitial volume may increase because of reduced entropy (7,8). Although this excluded volume effect may not be significant (9), it leads to a peak shift toward a higher elution volume. Therefore, the increase of injection volume results in increased Ve and consequently lowers the value of $[\eta]$. This effect is very pronounced at higher molecular weights for both polystyrene and styrene-n-butylmethacrylate copolymer. It has been shown by various workers (10-13) that as the thermodynamic quality of the solvent deteriorates, the concentration effect decreases. The concentration effect almost disappears in Θ-solvents. Most SEC work is done in thermodynamically good solvents and therefore the concentration effect cannot be avoided. To minimize this effect, use of lowest concentration that provides a chromatogram with 15-20 slices at 0.1 minute interval is recommended. It can be seen from Table 1 that at the lowest concentration the intrinsic viscosity value is within ±10% in all cases but two.

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