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CONCENTRATION DEPENDENCE IN GEL PERMEATION CHROMATOGRAPHY

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ABSTRACT

Four narrow distribution polystyrene samples with molecular weights from 3.5×10^4 to 2.7×10^6 and six linear or branched polyvinyl acetate samples were used in the study. GPC experiments were performed in two solvents (THF and MEK), three column sets (different permeation limits) and five different concentrations ranging from 0.05% to 3%.

The elution curves were normalized while average retention volumes and peak width were calculated. The data of the same sample with different concentrations can thus be compared on the same graph. The following conclusions were drawn.

(1) At very low concentration, elution curves were independent of the concentration. On increasing the concentration, peak positions were first moved to longer retention volumes and then the whole curves broaden appreciably.

(2) Concentration dependence increases with the increase in molecular weight and goodness of the solvent power.

(3) The plots of the retention volume vs concentration deviate from linearity. Extrapolation at higher concentrations is not reliable.

(4) The peak widths of the elution curves expressed by the variance σ increase with the increase of concentration.

(5) The initial slopes of the peak-concentration plot of the branched PVAc samples are proportional to the hydrodynamic volumes expressed as $[\eta] M$ of the samples.

INTRODUCTION

Gel permeation chromatography is the most widely used method for determining the molecular weight and molecular weight distribution of high polymers (1). The reliability of the results depends both on the correct manipulation of the experimental technique and on the appropriate ways of data treatments. Many experimental conditions such as concentration, rate of flow, injection volume and temperature will have significant effects on the chromatograms. It is necessary to make proper choice and control of these factors.

Because of their universality, differential refractive index detectors are commonly used to monitor the concentration of the polymer in the eluate. The sensibility of RI detector, however, depends strongly on Δn , the difference in refractive index of the polymer and the solvents. In certain cases, only a few solvents with unfavorable Δn are available. Chromatographers have to use higher concentrations in order to obtain larger signal. Therefore studies on the concentration dependence in GPC are essential both for theoretical and practical reasons.

The existence of concentration dependence in GPC was already reported in literature (2). Many experimental results showed that retention volume tends to increase with increasing concentration. The effect is more pronounced the higher the molecular weight of the polymer and on the solvent goodness. The origin of the occurrence of the concentration dependence in GPC was explained in different ways. Moore (3) explained it from a hydrodynamic point of view. Since there is a large difference in viscosity of the solution and solvent, the plug flow of the eluate will be perturbed and distortion of chromatogram shape and excessive tailing result. Janča (4,5) showed by theoretical calculation and experimental verification that 80-90% of

the concentration effect can be attributed to hydrodynamic factors. Recently the concentration effect has been explained thermodynamically as a consequence of the reduction of the effective hydrodynamic volume of the solvated polymer coil with increasing concentration (6,7). Both theories can explain qualitatively the concentration effect in GPC.

In this work, GPC experiments were performed on 4 narrow distribution polystyrene samples in three column sets with different permeation limits, five concentrations (0.05% to 3%) and two solvents (THF and MEK) respectively. In addition, six polyvinyl acetate fractions with different degree of branching were carefully selected so that three of them have nearly same intrinsic viscosities and the other three have nearly same \bar{M}_w . They were chromatographed in four different concentrations using THF as the solvent. All the chromatograms thus obtained were normalized and comparisons were made on the same sample at different concentrations. The effects of molecular weight, degree of branching, solvent, column sets and concentration on the peak retention volume, average retention volumes and peak widths were examined.

EXPERIMENTAL

Samples:

Four narrow distribution polystyrene samples with molecular weights of 2.7×10^6 , 6.7×10^5 , 2.0×10^5 and 3.5×10^4 were obtained from Waters Associates Inc. Six PVAc fractions were prepared and fractionated in this laboratory. The characterization data of these six PVAc samples are listed in Table 1.

Solvents:

THF, Analytical pure; MEK, Chemical pure.

GPC equipment:

TABLE 1
 Characterization Data For Six PVAc Fractions (8)

Sample	$\bar{M}_w \times 10^{-6}$	$[\eta]$	Conversion, %	G*	n_w^{**}
PVAc-1	2.10	282	65.8	0.673	8.46
PVAc-2	2.04	316	51.1	0.768	4.69
PVAc-3	2.07	361	21.8	0.871	1.71
PVAc-4	0.92	230	7.06	1	0
PVAc-5	1.14	230	43.8	0.84	2.22
PVAc-6	1.78	229	65.8	0.815	4.95

$$* G = [\eta]_b / [\eta]_l$$

** n_w characterizing the number of branches in one molecule.

Waters LC/GPC Model 244 chromatograph was used. Two of the three column sets consisting of two 1-meter column connected in series each were packed with deactivated porous silica gel prepared in this laboratory. The permeation limits of these two sets are 2.7×10^6 and 9.5×10^5 in PS molecular weight respectively. The third column is a commercial one consisting of one 50 cm Shodex-Pak A-80M with a permeation limit of 5×10^6 . In all cases, the flow rate was kept at 1 ml/min.

Data treatment:

All the chromatograms were normalized in order to make comparison on the same graph. The ordinates of the curves were transformed into $h_i / \sum h_i$, where h_i is the height of the species having retention volume of V_i . Figure 1 to Figure 6 are part of the typical curves obtained. Average retention volumes, \bar{V} , were calculated according to $\bar{V} = \sum (h_i V_i / \sum h_i)$. The widths of the curves were characterized by σ which were calculated

according to $\sigma = \sum [(h_i / \sum h_i) (v_i - \bar{v})^2]$. v_p vs c plots and \bar{v} vs c plots were illustrated in Figure 7 and σ vs c plot was shown in Figure 8.

RESULTS AND DISCUSSIONS

Concentration Dependence of GPC Chromatograms:

Chromatograms of four PS samples in five different concentrations (approximately 0.05%, 0.1%, 0.3%, 1% and 3%) with THF or MEK as the solvent were illustrated in Figure 1 to Figure 5. With the exception of the PS- 3.5×10^4 sample which has the lowest molecular weight, all the curves exhibit three different stages of variation of the shape on increasing the concentration of the sample. When the concentrations were sufficiently low, no concentration effect was seen and the curves coincide. This situation can be easily explained by both the hydrodynamic or the thermodynamic reasoning, since low concentration induces low viscosity difference and larger inter-molecular distances in the solution. On increasing the concentration to a certain level, the curves began to show distortion and the peaks moved to larger retention volumes. The spans of the chromatograms remained unchanged. This phenomenon can easily be realized through the theoretical consideration of reduction of coil dimension at finite concentration. The higher molecular weight portion of the sample will exhibit concentration effect at that concentration level while the lower molecular weight portion did not. As a result, the span of the chromatogram remained unchanged but the shape of the curves distorted. Elsdon (8) recently studied polydispersed samples and reached the same conclusion. On further increasing the concentration of the samples, the curves were broadened significantly along with severe tailing. This is obviously caused by very large difference in viscosity as well as

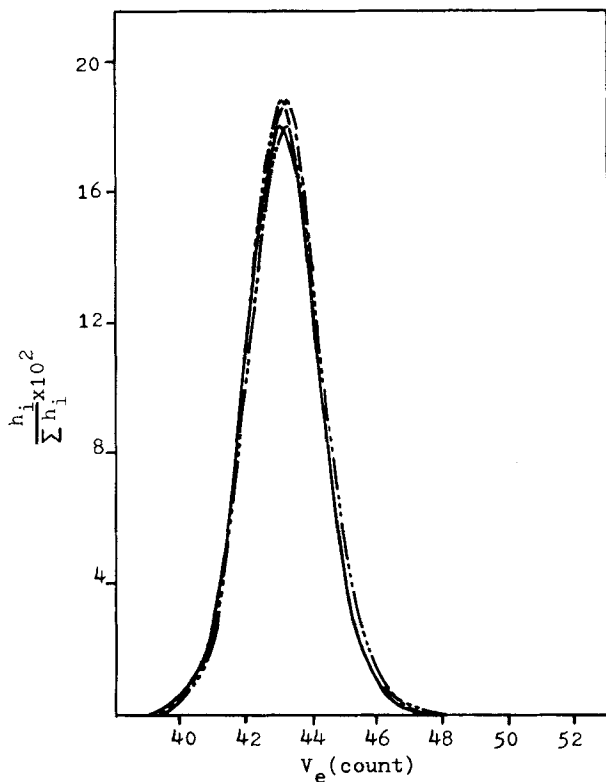


Fig. 1 Chromatograms of Five Different Concentrations of Sample PS- 3.5×10^4 in MEK

by the further reduction of coil dimension and overloading of the column. Figure 6 is the result of high performance GPC. Serious concentration effects were observed along with appreciable tailing.

Effects of Molecular Weight, Solvent and Column Type on the Concentration Dependence:

Molecular weight and goodness of the solvent are found to be closely related with the concentration dependence. From the normalized chromatograms obtained for four PS samples, certain classification can be made to

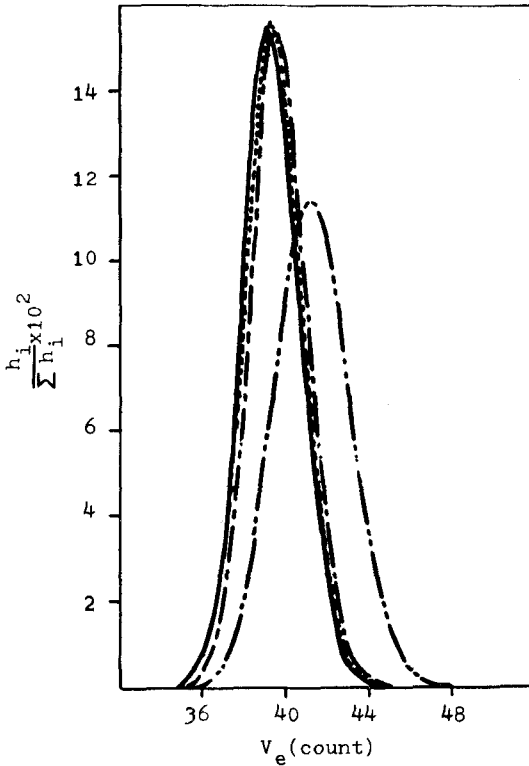


Fig. 2 Chromatograms of Five Different Concentrations of Sample PS-2.0 $\times 10^5$ in MEK

show different behavior in concentration dependence as illustrated in Table 2. It was shown that the concentration dependence increases with molecular weight and goodness of the solvent, in agreement with those reported in literature (2). The third and fourth vertical columns in Table 2 listed the concentration regions which showed respectively 'no concentration effect' and 'roughly beginning of the concentration effect'. The values of the fourth column should be quite close to the overlapping concentration c^* proposed by de Gennes in his scaling treatment of the polymer solution (9). Graessley (10)

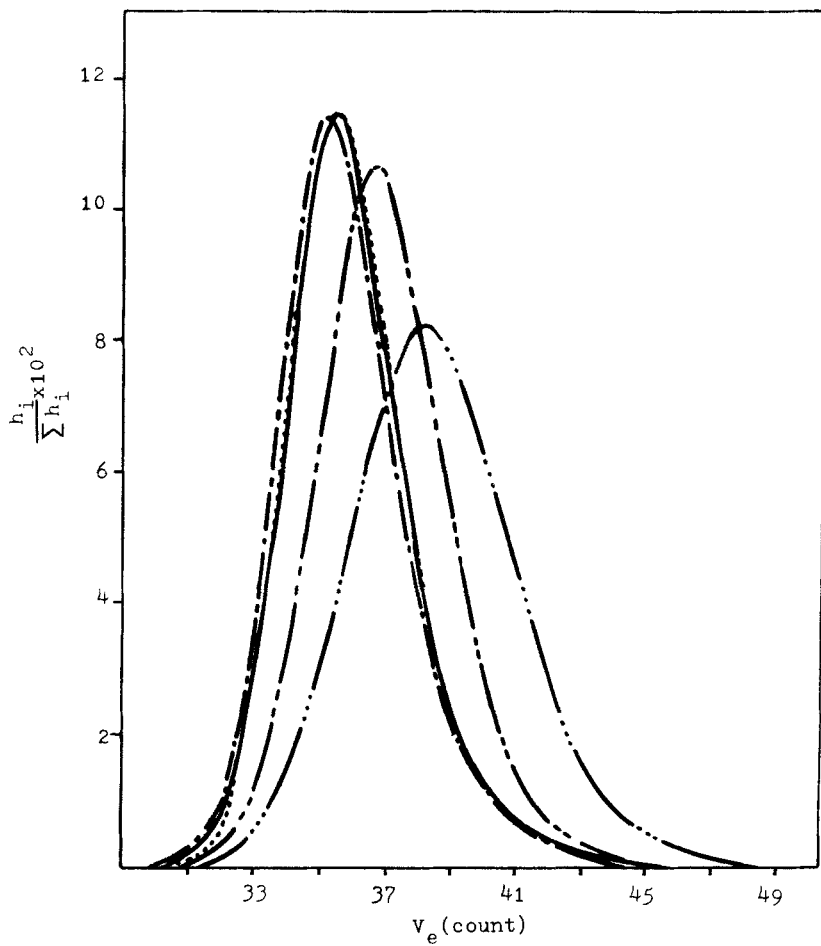


Fig. 3 Chromatograms of Five Different Concentrations of Sample PS- 6.7×10^5 in MEK

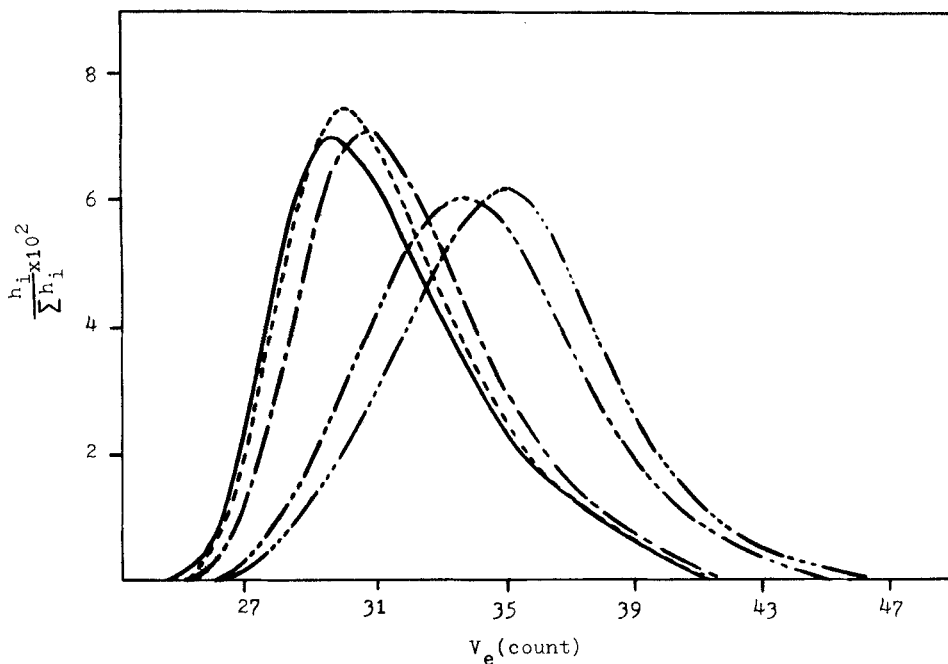


Fig. 4 Chromatograms of Five Different Concentrations of Sample PS-2.7 x 10⁶ in MEK

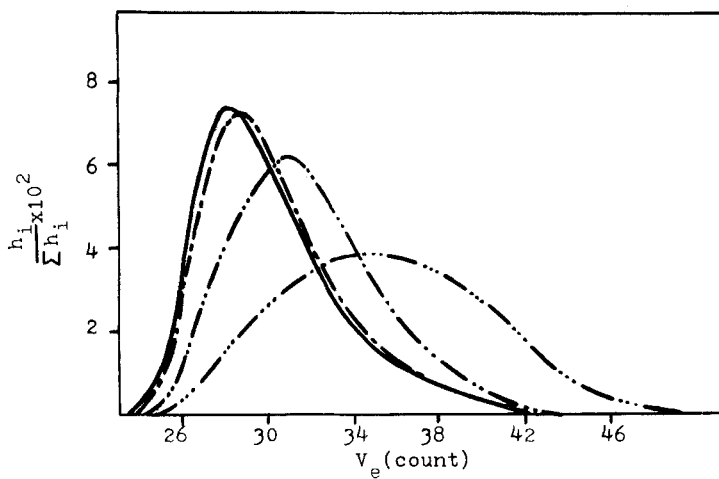


Fig. 5 Chromatograms of Five Different Concentrations of Sample PS-2.7 x 10⁶ in THF

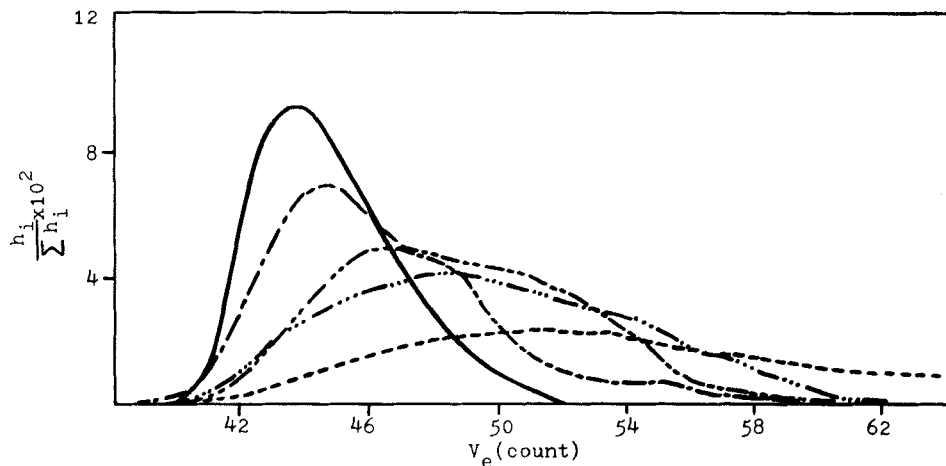


Fig. 6 Chromatograms of Five Different Concentrations From 0.01% to 3% of Sample PS- 2.7×10^6 in THF in Shodex-Pak A-80M Column

TABLE 2
Concentration Dependence of Four PS Samples

Sample MW	Solvent	No Conc. Effect, %	Distortion Span same, %	Broaden Tailing, %
2.7×10^6	THF, MEK	0.05; 0.1	0.3	1; 3
6.7×10^5	THF, MEK	0.05, 0.1, 0.3	1	3
2.0×10^5	THF	0.05, 0.1, 0.3	1	3
2.0×10^5	MEK	0.05, 0.1, 0.3, 1	-	3
3.5×10^4	THF	0.05, 0.1, 0.3, 1	-	3
3.5×10^4	MEK	0.05, 0.1, 0.3, 1, 3	-	-

TABLE 3
 c^* Values of 4 PS Samples in THF and MEK

Samples	$c^* \times 10^2$	
	THF	MEK
PS- 2.7×10^6	0.13	0.33
PS- 6.7×10^5	0.39	0.79
PS- 2.0×10^5	0.98	1.70
PS- 3.5×10^4	3.74	5.10

proposed a simple equation for calculating this overlapping concentration c^* as $c^* = 0.77 / [\eta]$. It will be interesting to see whether our experimental results correspond with those calculated theoretically. If the following Mark-Houwink equations are employed,

$$[\eta]_{\text{THF}} = 0.682 \times 10^{-2} M^{0.766}$$

$$[\eta]_{\text{MEK}} = 1.95 \times 10^{-2} M^{0.635}$$

the values of c^* calculated for the four PS samples are listed in Table 3. Comparison of the values of the 4th column in Table 2 with those in Table 3 show that the agreement is good in the case of THF and fair in the case of MEK.

Figure 7 gives the plot of V_p and \bar{V} against concentration for different molecular weight and different solvents. Only sample PS- 3.5×10^4 gives linear plot. Plots of other samples with higher molecular weight deviate from linearity in higher concentrations. Suggestions in literature of eliminating concentration dependence by extrapolation to infinite dilution are not justified by our data. The influence of concentration effect on the curve width was shown in Figure 8. In all cases, the curve width expressed with σ increases with the increase of concentration.

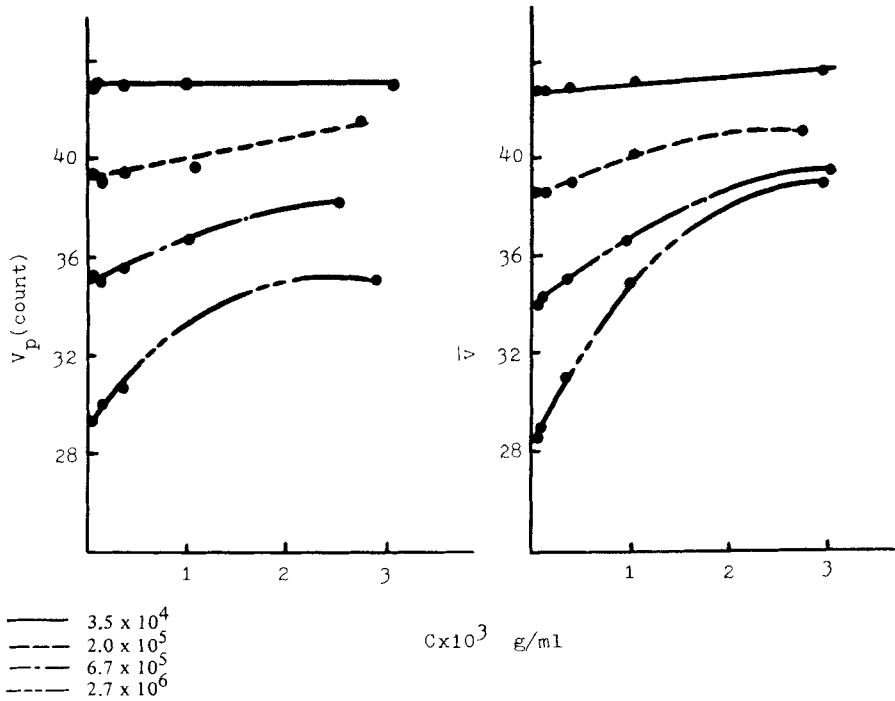


Fig. 7 V_p vs C Plots of Four PS Samples in THF (Right) and in MEK (Left)

Concentration Dependence of Branched Samples:

Concentration effects on the GPC studies of branched polymers have not been reported in literature. Since difference in degree of branching induces difference in segmental densities of the samples in solution which will have significant effect on the concentration dependence of the GPC behavior. V_p vs c plots for the three branched PVAc samples with nearly same intrinsic viscosities and the other three with nearly same \bar{M}_w were illustrated in Figure 9 and Figure 10. It is obvious that when the concentrations were below 0.6%, V_p vs c plots were linear with different slopes for different samples. Since these six samples represent different degree of branching, the

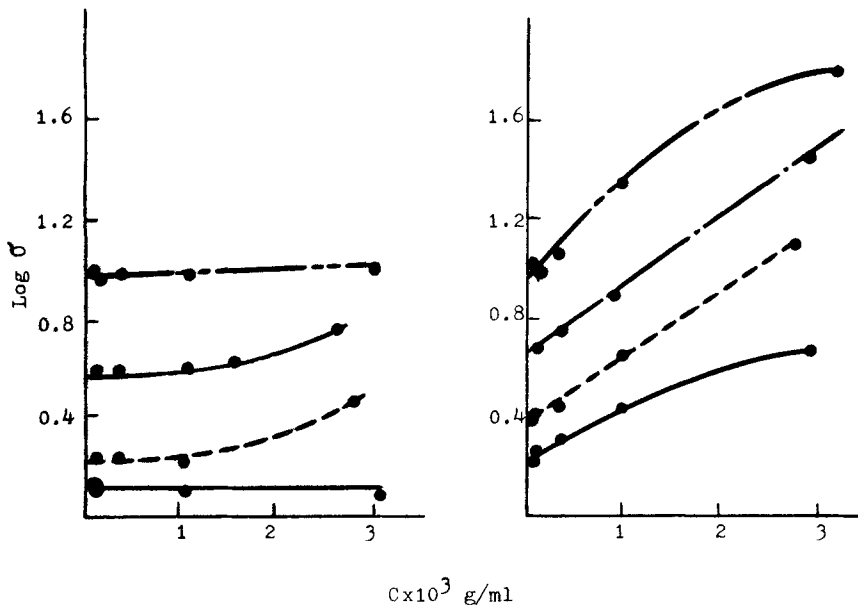


Fig. 8 $\text{Log } \sigma$ vs C Plots of Four PS Samples in THF (Right) and in MEK (Left)

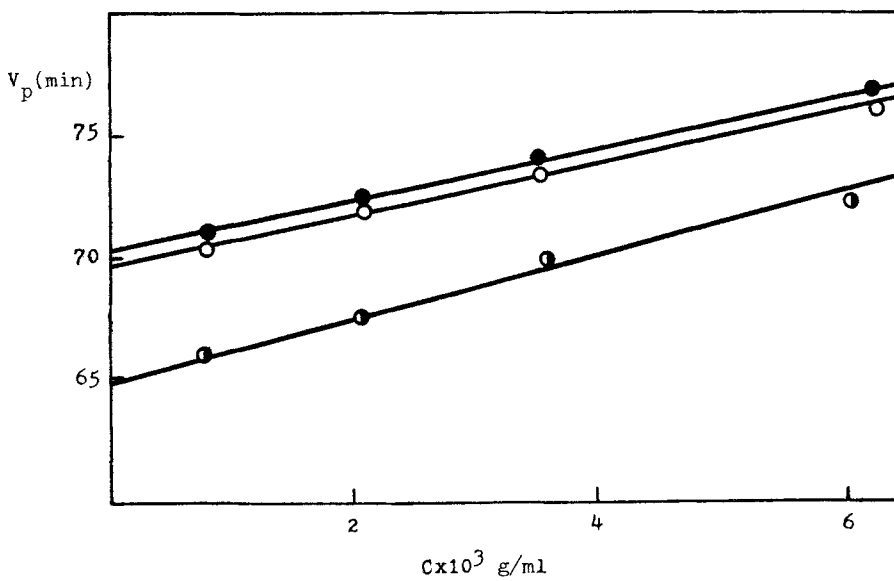


Fig. 9 V_p vs C Plots of Three PVAc Samples With Nearly Same $[\eta]$

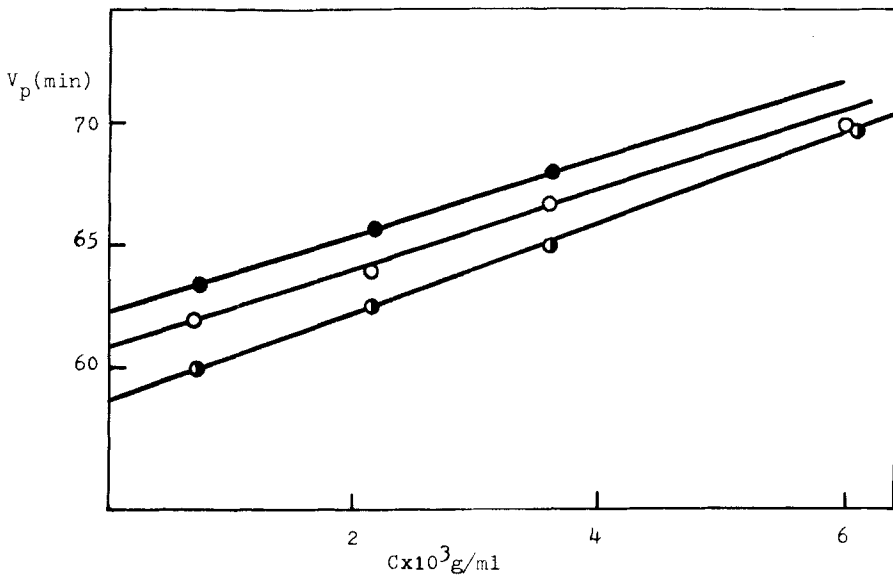


Fig. 10 V_p vs C Plots of Three PVAc Samples With Nearly Same \bar{M}_W

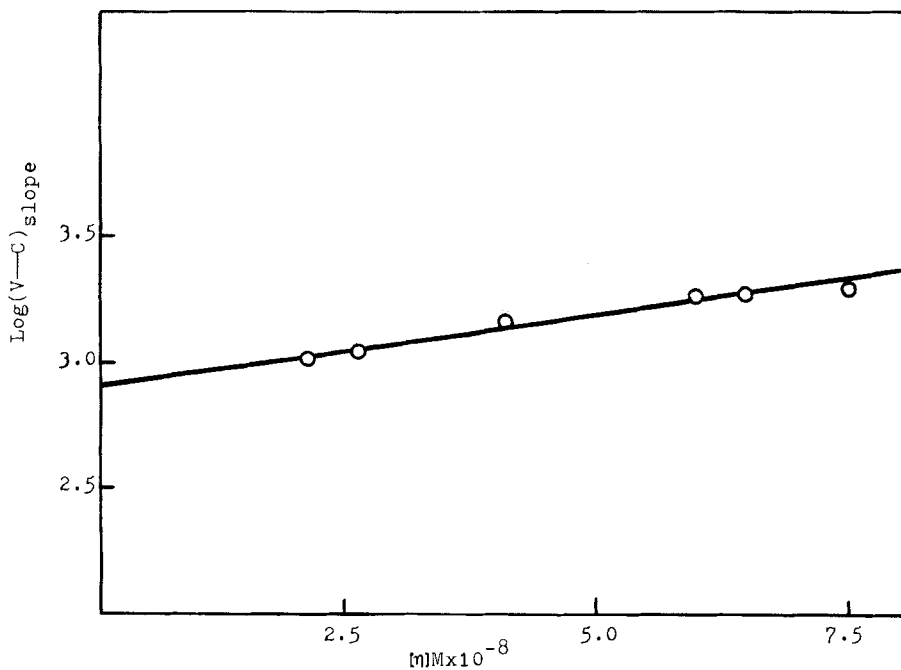


Fig. 11 $\text{Log}(V-C)_{\text{slope}}$ vs $[\eta] \bar{M}_w$ Plots for Six PVAc Samples With Different Degree of Branching

concentration effect should be different. If we take the slope of the V_p vs c plot as an indication of magnitude of concentration dependence, we found that these slopes depend on the hydrodynamic volumes, $[\eta]^M$, of the samples. Figure 11 illustrates the slope vs $[\eta]^M$ plots which gives a good straight line. From our data, it can be concluded that the concentration dependence of GPC behavior for branched samples of different degree of branching can still be realized through the variation of the hydrodynamic volume.

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