Concentration Dependence of Elution Volumes in size Exclusion Chromatography of Polymer Molecules. II. Poly(Methyl Methacrylate) in Ideal Solvent

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CONCENTRATION DEPENDENCE OF ELUTION VOLUMES IN SIZE EXCLUSION CHROMATOGRAPHY OF POLYMER MOLECULES. II. POLY(METHYL METH-ACRYLATE) IN IDEAL SOLVENT

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ABSTRACT

The concentration effects occurring in size exclusion chromatography of polymer molecules have been investigated for the case of elution of macromolecules in an ideal solvent. It is shown that increases in the elution volumes with polymer concentration are detectable with the high efficiency columns employed. The concentration dependence of elution volumes is much lower than that previously determined with good solvents. The main factor contributing to the shift of elution volumes seems to be the viscosity of the polymer solutions, but another effect appears also to be present. This latter effect possibly suggest that in semi-concentrated solutions of polymer molecules in ideal solvents a continuous contraction of the polymer chains occurs, below their unperturbed dimensions, similar to that happening when the temperature of ideal solutions is decreased. More investigation on this point is needed.

INTRODUCTION

The increase of the elution volumes with sample concentration occurring in size exclusion chromatography (SEC) of polymer molecules has been mostly attributed either to the sole effect of contraction of the polymer coils with increasing concentration [1-3] or to a sum of contributing processes among which, in addition to the former effect, the frictional forces in the column interstitial volume (viscosity effect) seem to play the most important role [4-6].

The viscosity effect can be isolated and experimentally seen by eluting polymer samples which do not permeate the packing pores but flow in the interstitial volume only [4]. On the other hand, it is not possible to devise a chromatographic experiment where the viscosity effect is certainly not operative and the coil contraction alone takes place. Therefore, it is a difficult task to establish the presence and the relative importance of the different effects contributing to the total concentration dependence of the elution volumes of polymer molecules eluting in the permeation range of the chromatographic columns.

The semi-empirical and theoretical models proposed for the interpretation of the concentration effect in SEC are mainly based on the change of coil size with increasing polymer concentration in solution [1,7,8] and on relationships between the extent of the concentration effect and the thermodynamic nonideality of the polymer solutions [9,10].

The only theory of concentration effects which explicitly takes into account the viscosity effect as well is the one by Janca [6]; this theory was later generalized to include the contribution of the so-called secondary exclusion [11]. The application of such a theory to some experimental data [6] led to an estimation of the viscosity effect as responsible of approximately 80% of the total shift in the elution volumes of polymer molecules permeating the column pores. Such a result was found to be virtually independent of the concentration and of the amount of the injected solutions, as well as of the column efficiency. On the contrary, by increasing the column efficiency the overall concentration dependence of the elution volumes increased.

In a previous paper [12] we proposed a practical experimental procedure for the evaluation of the ratio of the viscosity contribution to the total concentration effect. The method stands on the assumption that no other phenomena, beside viscosity and coil contraction, contribute to the total concentration effect. It is also assumed that the same viscosity contribution occurs for solutions of permeating and of totally excluded polymer molecules having the same specific viscosity. In other words, the total concentration effect for the former solutions should be higher than for the latter ones, the difference being entirely due to the effect of coil contraction. The application of this method to the case of elution of narrow distribution polystyrene molecules in a good solvent showed

[12] that both viscosity and coil contraction contributions are important, the latter one being the principal responsible of the total concentration dependence of the polymer elution volumes.

In this paper the results are reported for polymer molecules eluted in a thermodynamically poor solvent. In poor solvents, the concentration effect is reduced because of the lower viscosities of the polymer solutions and the reduced possibility of contraction for the dissolved macromolecules: actually, one might foresee that in the limit of an ideal solvent, where the molecules are at their unswollen, unperturbed, dimensions, only the viscosity effect should occur. The choice of a thermodynamically ideal eluent for SEC experiments is complicated by the facts that frequently such an eluent has a low polarity (e.g. cyclohexane at 35 °C for polystyrene), with the consequence of possible polymer adsorption on the stationary phase, and that often it is a mixture of solvents and makes likely the occurrence of secondary phenomena, such as preferential solvation and/or adsorption.

The system which has been choosen for the present study is constituted by poly(methyl methacrylate),(PMMA), in 2-ethoxyethanol. 2-Ethoxyethanol is practically an ideal solvent for PMMA at room temperature [14] and has high polarity, which makes it a suitable eluent in order to avoid polymer adsorption on the silica gel columns [15] employed throughout the measurements of the concentration effects.

EXPERIMENTAL

Narrow distribution PMMA standards (Polymer Laboratories, Shrewsbury, England) were eluted with a Waters M45 pump on two different column combinations: the first one consisted of 2 columns (25 cm length, 0.46 cm I.D., each) packed with microparticulate silica gels (LiChrospher, E. Merck, Darmstadt, W. Germany) having mean pore sizes of 100 nm and 50 nm respectively; the second one was made with 2 similar columns, respectively packed with LiChrospher of 10 nm mean pore size and with a large pore volume silica gel, SG-7G, kindly gifted by Dr. Dusan Berek (Polymer Institute of the Slovak Academy of Sciences, Bratislava, Czechoslovakia). A Siemens differential refractometer as a detector and a Rheodyne 7010 valve with a 10 μl loop to introduce the samples into the columns were employed. The solvent for PMMA samples, as well as the chromatographic eluent, was analytical grade 2-ethoxyethanol (C. Erba, Milano, Italy). The elutions were performed at a constant flow rate of approximately 0.5 cm^3/min; all the measurements were done in triplicate and the results averaged.

RESULTS AND DISCUSSION

The calibration curve of the first column system (100 nm + 50 nm) is shown in Fig. 1. The available PMMA sample of highest molar mass (640000) still elutes in the separation range of the
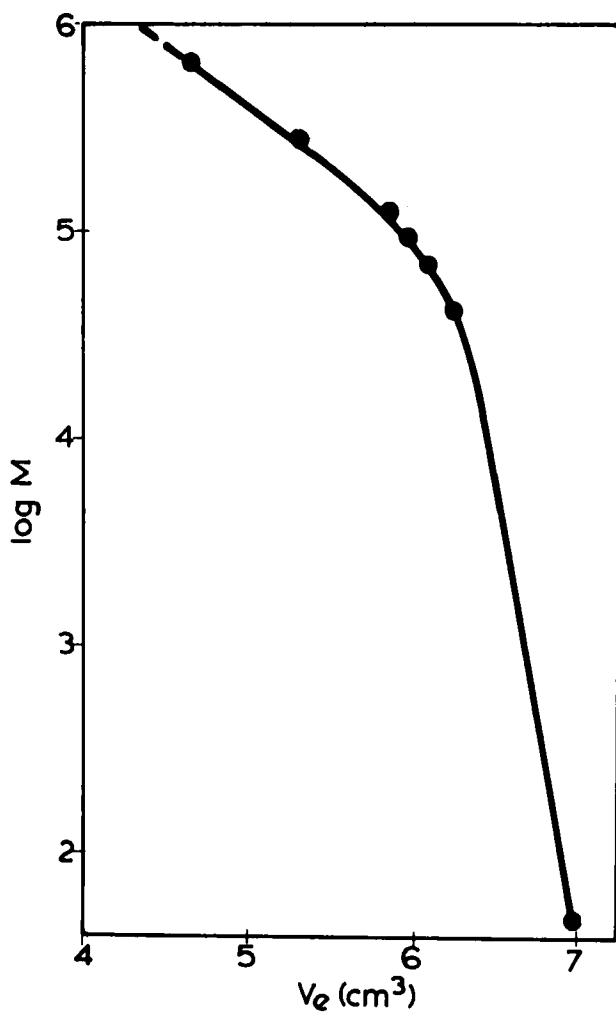
FIGURE. 1   Calibration curve of the column system 100 nm + 50 nm for
PMMA in 2-Ethoxyethanol.

columns; therefore, for this column system, it was not possible to obtain the elution volumes of excluded polymer samples from which to evaluate the viscosity contribution to the total concentration effect. The concentration dependences of elution volumes were nevertheless measured for three different PMMA standards (molar masses 128000, 280000 and 640000) in order to compare the extent of the phenomenon with that obtained, on the same columns,[12] with polystyrenes dissolved in a good solvent. In Fig. 2 the experimentally observed elution volumes are plotted against the injected polymer concentrations: one can see that increases of elution volumes do occur, though to a much lower extent than those previously reported for polystyrene in tetrahydrofuran [12].

The total increment of elution volumes $\Delta V_t = (V_{e,c} - V_{e,o})$, where $V_{e,c}$ is the polymer elution volume at concentration c and $V_{e,o}$ is the polymer elution volume extrapolated at c=0, are plotted in Fig. 3 against the polymer specific viscosities. The specific viscosities were calculated by means of the Huggins equation

$$\eta_{sp} = [\eta] \, c + k_H [\eta]^2 \, c^2$$

where k_H is the Huggins constant, the concentration c is expressed in g/cm^3 and $[\eta]$ is the polymer intrinsic viscosity obtained from the Mark-Houwink equation relative to PMMA in 2-ethoxyethanol [14]:
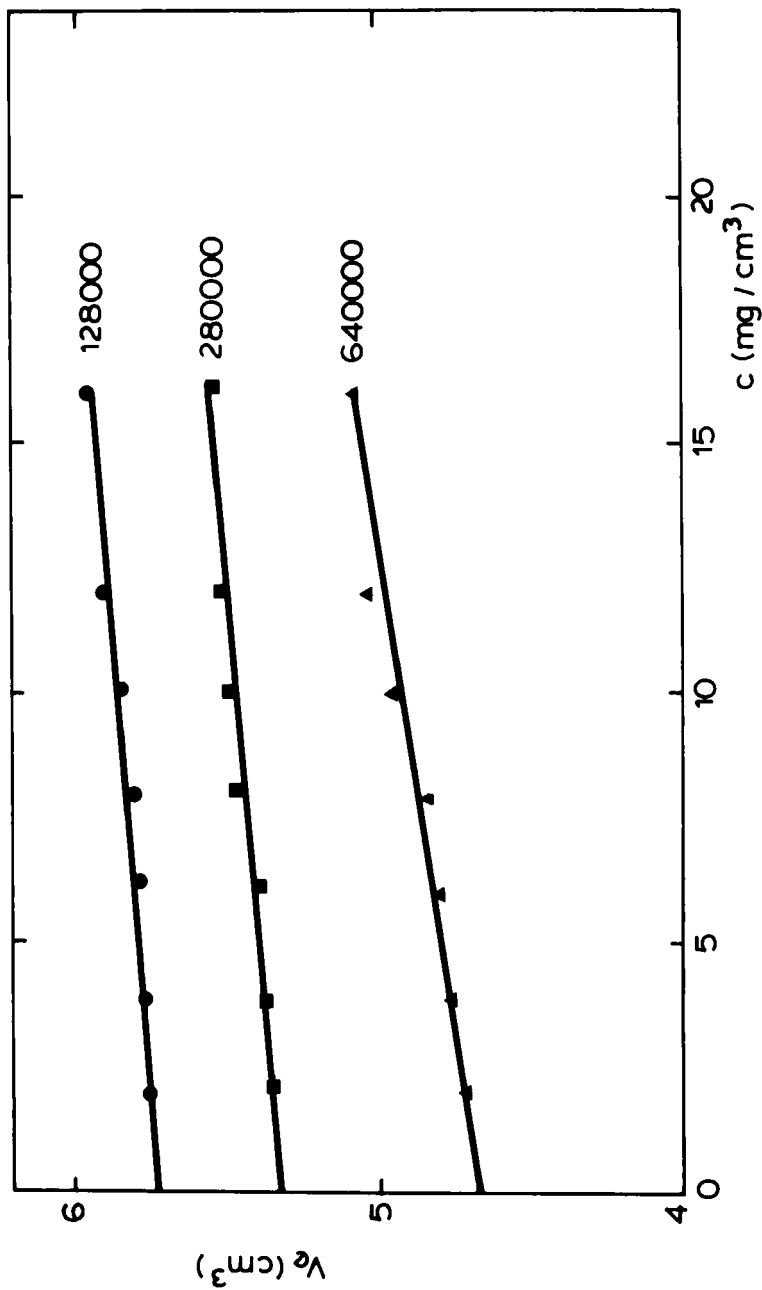
$$[\eta] = 5.00 \ 10^{-2} \, M^{0.5}$$

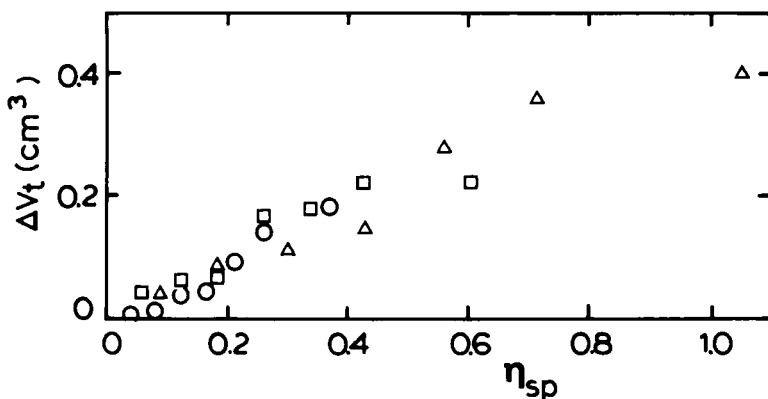FIGURE 2. Elution volumes of PMMA standards at different concentrations in the column system 100 nm + 50 nm.

FIGURE 3.   Changes of elution volumes, ΔV_t, with specific viscosities.
Columns 100 nm + 50 nm. $\triangle$: PMMA 640000; $\square$: PMMA 280000;
$\bigcirc$: PMMA 128000.

Huggins   constants k_H,   for   PMMA in 2-ethoxyethanol are
not   reported   in   the   Literature;   however   by   analogy with the
values   reported   [16,17]   for   other   single   and mixed ideal
solvent   systems,   the   value $k_H=1$ can be reasonably used for
all the PMMA samples investigated.

If   the total increase of elution volumes of Fig. 2 were only
due   to   the   viscosity   contribution, the points on Fig. 3 should
lie   on   a   common   straight line. Unfortunately, the experimental
data   of   Fig. 3 are quite scattered; it seems however possible to
say   that   the   viscosity   effect   is   indeed the main factor, but
possibly   not   the   only   one,   in   determining   the   shift in the
elution volumes.

The   calibration   curves   with   polystyrene   samples   in
tetrahydrofuran   of the individual colums of the second column set
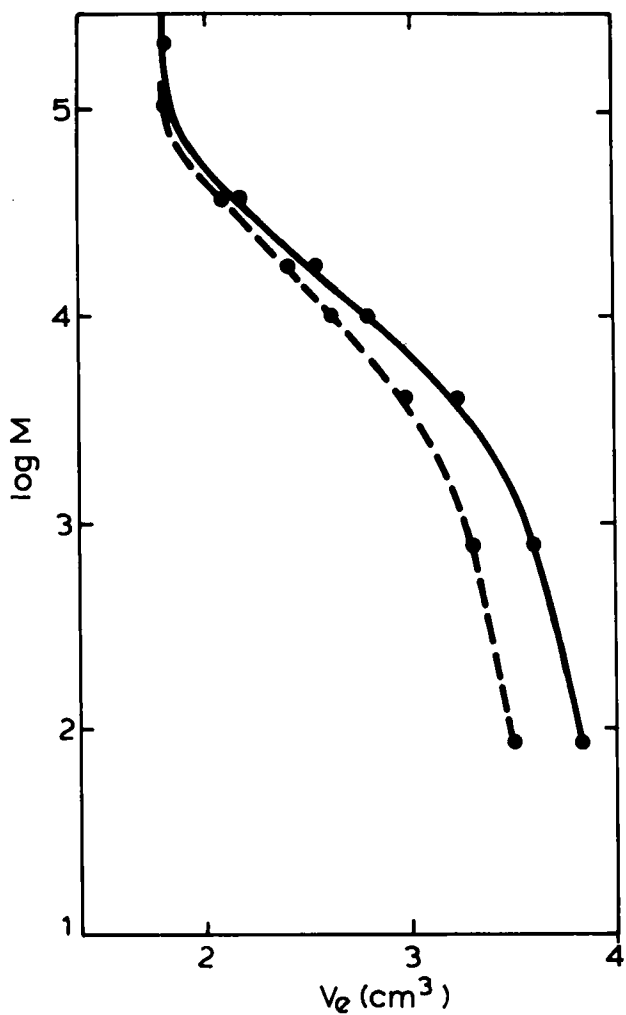used   in   the   present   investigation   are   shown   in   Fig. 4. The

FIGURE 4.   Calibration curve with PS standards in tetrahydrofuran for
the columns 10 nm (- - -) and SG-7G (———).

calibration   curve   of   the   2-column   set   with   PMMA   in
2-ethoxyethanol is shown in Fig. 5. One can see that in this case
the highest molecular mass PMMA sample (M = 640000, log M= 5.806)
has an elution volume outside the column separation range.
Therefore the experiments performed with the second column system
allow for the measurement of the pure contribution from the
solution viscosities to the increase of the elution volumes by
increasing concentrations. The concentration dependences of the
elution   volumes   of   three   permeating   samples   (45200,   72000,
128000) and of the excluded one are plotted in Fig. 6. After
calculation of the specific viscosities as previously described,
the total increments of elution volumes are reported in Fig. 7 as
a   function   of η_{sp}.   The   increase $\Delta V_{t,ex}$ of   elution
volumes of the excluded sample, PMMA 640000, is due to the
viscosity contribution occurring in the interstitial volume of
the columns. One can see that, for the permeating polymers, an
additional small change of elution volumes occurs, therefore
indicating that the effect of the viscosity is not the only one
taking place in the system.

For each of the permeating polymer samples the contribution from
viscosity, ΔV_{η} , to the total concentration effect ΔV_{t}
is given, at each concentration, by the $\Delta V_{t,ex}$ of the
excluded PMMA sample at the same η_{sp} value. The ΔV_{t}
and ΔV_{η} values relative to the permeating polymers at the
different injected concentrations are shown in Fig. 8, where it
is now evidentiated that of the total (small) change of elution
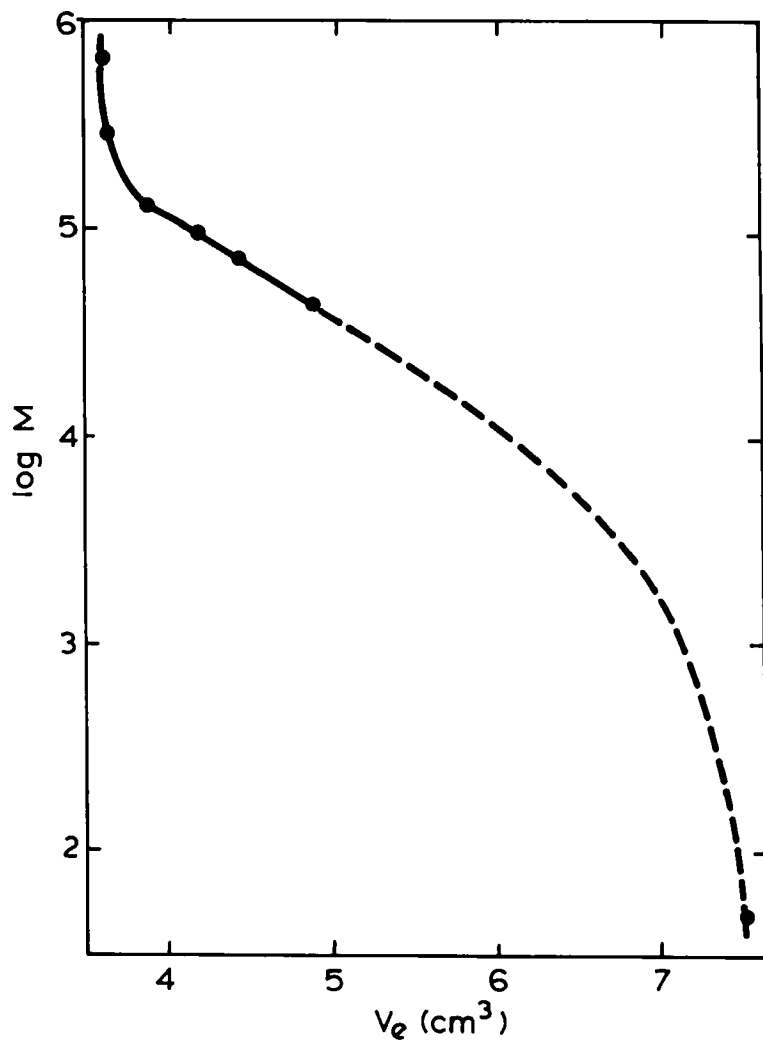
FIGURE 5.   Calibration curve for PMMA in 2-Ethoxyethanol of the column
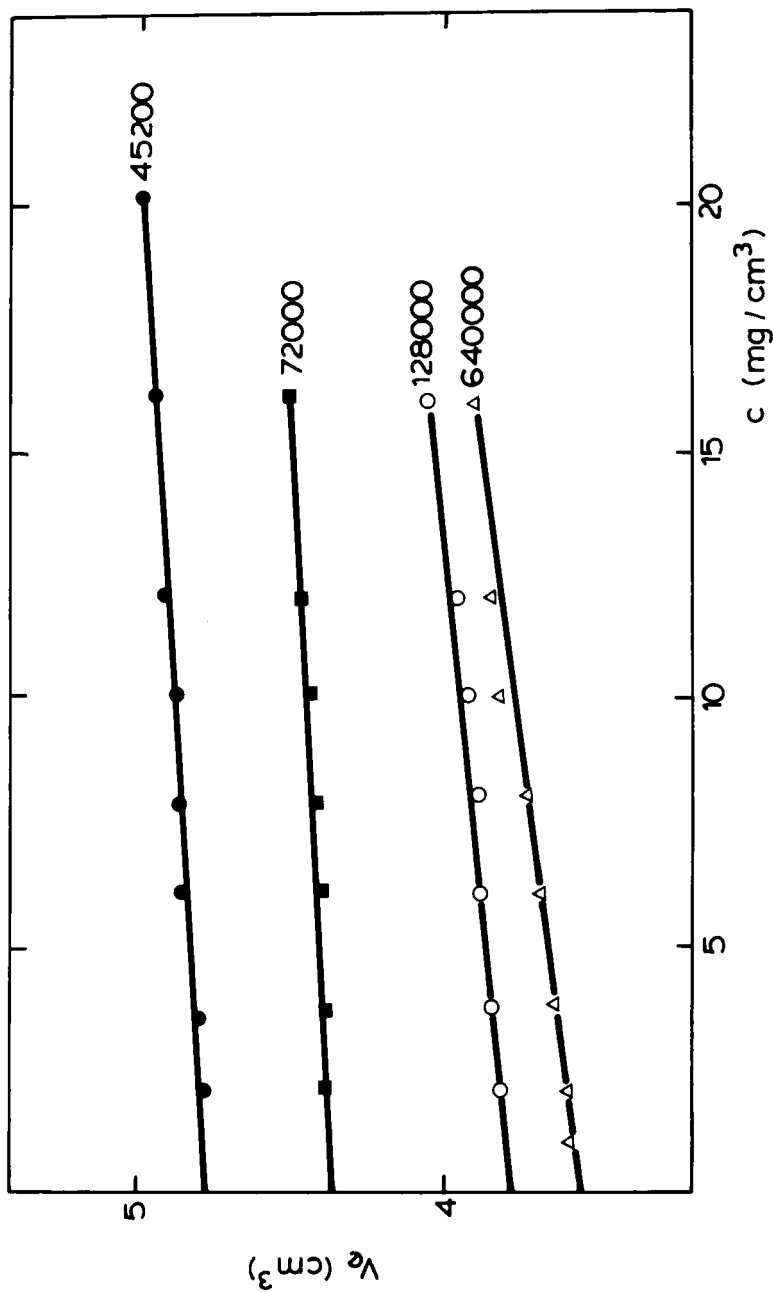   system 10 nm + SG-7G.

FIGURE 6. Elution volumes of PMMA standards at different concentrations in the column system 10 nm + SG-7G.
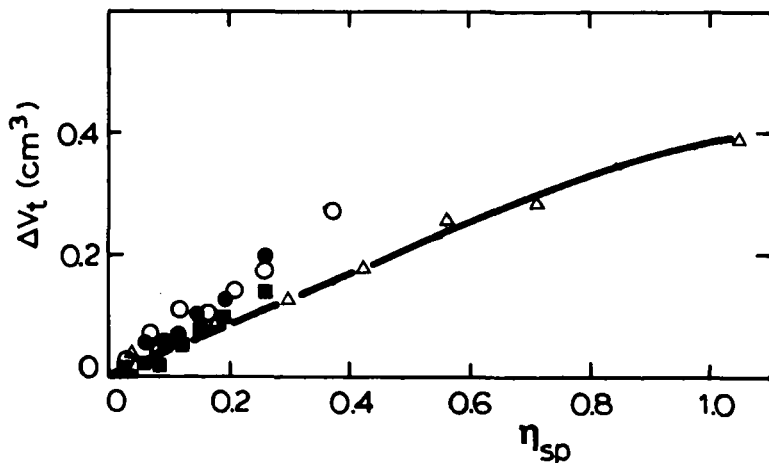
FIGURE 7.   Changes of elution volumes, ΔV_t, with specific viscosities.
            Volumes of 10 nm + SG-7G. $\triangle$: PMMA 640000; O PMMA 128000;
            ■ : PMMA 72000; ● : PMMA 45200.

volumes, the effect due to the viscosity of the polymer solutions

is the major one. From the ratio of the slopes, $(d(\Delta V_\eta)$ /

dc)/(d(ΔV_t) / dc), of the straight lines drawn in Fig. 8,

the average relative contributions to the total concentration

effect due to the viscosity are calculated to be 62% for PMMA

45200, 81% for PMMA 72000 and 60% for PMMA 128000.

The above results show that in the thermodynamically ideal

system PMMA/2-ethoxyethanol, where the polymer molecules should

reach their unperturbed dimensions, some other effect in addition

to the viscosity one takes place in giving the increase of

polymer elution volumes with concentration. We have assumed,

throughout this work and the previous one [12] that no other

phenomena contributes to the concentration effect, beside the
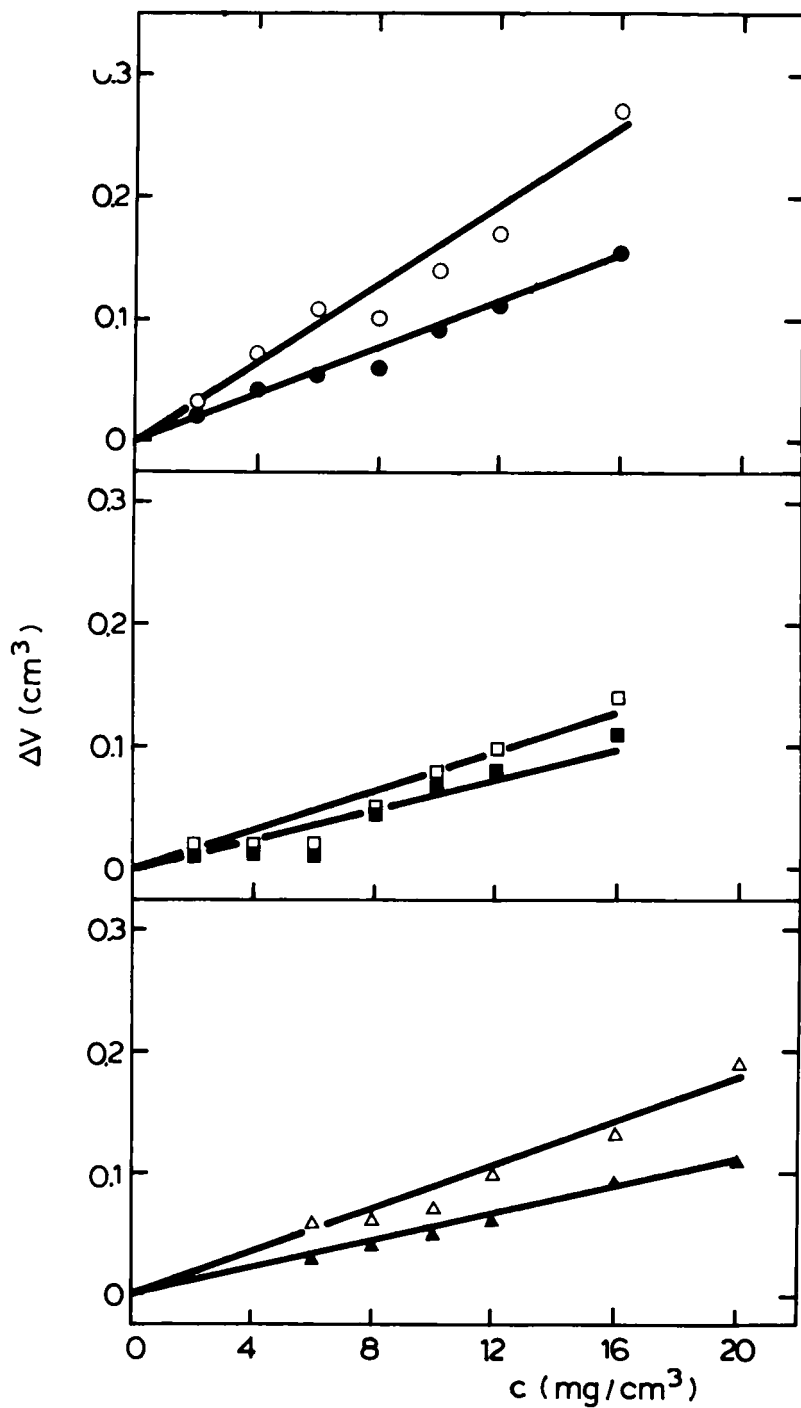
FIGURE 8. Changes of elution volumes with concentration in the columns 10 nm + SG-7G. PMMA 128000: $\bigcirc$, $\triangle V_t$; $\bullet$, $\triangle V_\eta$. PMMA 72000: $\square$, $\triangle V_t$; $\blacksquare$, $\triangle V_\eta$. PMMA 45200: $\triangle$, $\triangle V_t$; $\blacktriangle$, $\triangle V_\eta$.

viscosity and the change of dimensions of the polymer coils. It

has already been shown [15] that in the limit of vanishing

polymer concentration no adsorption of the PMMA molecules takes

place on the silica substrate when 2-ethoxyethanol is used as

eluent; therefore the possibility of polymer retardation by

enthalpic interactions can be ruled out also for the more

concentrated solutions of this work. In a comment by Janca

[18] about our previous results on the concentration effects

of polystyrene in tetrahydrofuran [12], it was suggested that

some other phenomenon was also operative in determining the whole

change of elution volumes with concentration: it is not possible

to establish whether this different, unknown, contribution is the

same as that shown in this paper. However, to explain the

behaviour of PMMA in 2-ethoxyethanol, we might also take into

account that, with solutions of polymer molecules in a

thermodynamically ideal solvent, the effect of increasing the

polymer concentration could be comparable with that occurring

when the temperature of ideal solutions is decreased and a

continuous contraction of the polymer chains [19] below their

unperturbed dimensions is found. In the latter case, the flexible

macromolecules are seen to shrink below the unperturbed

conformation to reach a much more compact situation. For PMMA

molecules more coiled structures than in other ideal solvents

were found in acetonitrile [20], and were attributed to the

capacity of the solvent of promoting intramolecular aggregation.

A similar effect might occur when the polymer concentration of

the ideal solutions is increased. Further investigations will be carried out to clarify this point.

In conclusion, the concentration dependence of polymer elution volumes in SEC has been found to be detectable also in a thermodynamically ideal solvent, though it is much lower than that observed in good solvents. In such a system, the main cause of the shift of elution volumes appears to be the viscosity of the polymer solutions, but a small additional contribution is also seen to be present. At the moment, it seems not possible to evaluate with certainty the origin of this latter contribution, especially in the absence of data on the macromolecular conformations in semi-concentrated solutions in ideal solvents.

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