Concentration dependence of chain dimensions and its role in gel chromatography

T. Bleha, J. Mlýnek and D. Berek
Polymer Institute, Slovak Academy of Sciences, 809 34 Bratislava, Czechoslovakia
(Received 24 September 1979; revised 29 November 1979)

A theoretical model has been developed for the concentration effect in gel chromatography, i.e. the dependence of the elution volume V_e on the concentration of injected polymer c. On the basis of the theoretical relations of Yamakawa and Eizner for coil shrinkage with increasing concentration in the range of dilute polymer solutions, relations predicting the extent of the concentration effect have been derived. A comparison of the calculated and experimental data for polystyrene in tetrahydrofuran and toluene has shown that both theories slightly underestimate the extent of the concentration effect but qualitatively correctly describe its dependence on molecular mass M and on thermodynamic quality of an eluent given by the product A_2M, where A_2 is the second virial coefficient of the polymer–eluent system. The proposed model explains the recently established correlation between the slope of the concentration dependence of V_e and the thermodynamic quality of the eluent and theoretically accounts for the method for estimating the coefficient A_2 from gel chromatographic measurements. The possibility of using the measurements of concentration effects for examining the reliability of the theoretical relations for coil shrinkage with concentration in dilute polymer solution as well as for eventual semiempirical modification of these relations is examined.

INTRODUCTION

In infinitely diluted polymer solutions, dimensions of macromolecules have been characterized in detail both experimentally and theoretically. Less information is available concerning solutions with finite concentration.

From the theoretical point of view, the concentration dependence of mean macromolecular dimensions remains a provoking problem, incorporating complicated intra- and inter-molecular effects of the excluded volume. Several authors have presented theoretical relations[1–5] describing changes in macromolecular dimensions with concentration over the range of dilute solutions. The concentration effect has been estimated also by a computer simulation[6,7] using the Monte Carlo method. All these approaches agree qualitatively that polymer coil dimensions should decrease with increasing polymer concentration in solution. It is most often assumed that as the concentration increases, considerable interpenetration of polymer coils occurs. In the limiting case of an amorphous polymer, the polymer coils have the same dimensions as in a θ solvent. Only a small number of direct experimental measurements of concentration changes in macromolecular dimensions have been published[8–11]. All are based on small-angle X-ray or neutron scattering methods and concentrate mainly on the region of semi-diluted and concentrated solutions.

The problem of macromolecular dimensions in diluted solutions at finite concentrations is connected closely with the 'concentration effect' in gel chromatography (g.p.c.), i.e. the shift of the peak elution volume V_e to higher values with increasing concentration of an injected polymer. The higher the solute molecular mass, the lower its polymolecularity, and the better the solvent, the more pronounced is the shift[12–17]. Rudin[18,19] proposed a semi-empirical model for the interpretation of the concentration effect in g.p.c., based on the idea of coil shrinkage with increasing polymer concentration in solution. He assumed that the dominating mechanism in g.p.c. is separation due to different sizes of solute molecules. In the g.p.c. method, the smaller the molecular dimensions of solute (expressed by their effective hydrodynamic volume V_h), the greater is the elution volume V_e. If the increase in the polymer concentration is accompanied by a decrease of size and V_h of macromolecules, V_e should in turn increase; and this is observed.

By systematic study of the concentration effect in our laboratory[15,16,20,21] we have found that the concentration effect could be used for estimating the second virial coefficient of the polymer–eluent system[16]. In the present paper, the theory of the concentration effect has been formulated. The theory is based on theoretical relations[1–5] describing variations of chain dimensions with concentration. The resulting relations predict V_e as a function of polymer concentration and parameters of the polymer–solvent interaction. Comparison of the theoretical prediction and experimental results might serve as an approximate criterion of the correctness of individual theoretical expressions for coil shrinkage with concentration[1–5] in the range of dilute solutions.

THEORETICAL MODEL

The relations presented by Eizner[2] and Yamakawa[3] have been chosen to express macromolecular compression with increasing polymer concentration c in solution. The Eizner

0032–3861/80/070798–07$02.00

theory is based on a smoothed-density model for dilute polymer solutions and describes the dependence of the expansion factor of the radius of gyration $\alpha_s^2 = \overline{s^2}/\overline{s_0^2}$. $\overline{s_0^2}$ is the radius of gyration of the coil in the unperturbed state. The concentration dependence of α is expressed[2] by a power series:

$$\alpha_c = \alpha_0(1 - A_2MF_Ec - A_3MF'_Ec^2 - \cdots) \qquad (1)$$

where M is the relative molecular mass, A_2 and A_3 are, respectively, the second and third virial coefficients of the polymer–solvent system and F_E and F'_E are complicated functions of the parameters of the excluded volume. Eizner has also shown that, in the range of low concentrations, the contribution of the quadratic term on the right hand side of equation (1) is negligible and the expansion factor decreases linearly from the limiting value for infinite dilution.

Yamakawa[3] derived a closed analytical expression for the concentration dependence of the expansion factor for the end-to-end distance $\alpha_h^2 = \overline{h^2}/\overline{h_0^2}$ by solving differential equations for distribution functions of end-to-end distances. After rearranging Yamakawa's relation we have[3,22]:

$$\alpha_c = \alpha_0 \exp[-A_2MF_Yc] \qquad (2)$$

When rearranging equation (2), the binary cluster integral β of the segment–segment interaction was expressed[22] by A_2. The function F_Y is defined as:

$$F_Y = (K/k_1)\,[1 - h_0(\bar{z})_0]/h(\bar{z}_0) \qquad (3)$$

where $\bar{z}_0 = z/\alpha_0^3$, z is the parameter of the excluded volume. The constants K and k_1 have the values of 0.4551 and 5.731 respectively[22]. For the sake of simplicity, the function $h(\bar{z}_0)$ was taken to be $h_0(\bar{z}_0)$ because the series expansion according to $\bar{z}_0$ indicates[22] negligible difference.

We introduce an approximation of a polymer coil in solution to a sphere, the effective hydrodynamic volume of which in infintely dilute solution is $V_h(0)$:

$$V_h(0) = (4/3)\pi(\overline{s^2})^{3/2} = (4/3)\pi([\eta]\,M/\Phi') \qquad (4)$$

where $\Phi' = 100\,(6)^{3/2}\Phi$ and Φ is the Flory coefficient[23] varying with the quality of the solvent in agreement with[24]:

$$\Phi' = \Phi'_\theta\,(1 - 2.63\,\epsilon + 2.86\,\epsilon^2) \qquad (5)$$

$\epsilon = (2a - 1)/3$ and a is the exponent from the relation for the limiting viscosity number $[\eta] = KM^a$. The hydrodynamic volume from equation (4) is expressed by parameters for the θ state and by the expansion factor α_0. Since $[\eta] = K_\theta M^{1/2}\alpha_0^3$ by substituting into equation (4), we obtain:

$$V_h(0) = (4\pi K_\theta M^{3/2}/3\Phi'_\theta)\,[\alpha_0^3/(1 - 2.63\epsilon + 2.86\epsilon^2)] \qquad (6)$$

where the terms in the first bracket on the right of equation (6) determine V_h under θ conditions. The value of 4.2×10^{24} is recommended[23] for the constant Φ'_θ. Substituting α_0 for α_c from equations (1) and (2) in the last equation gives the expression of the effective hydrodynamic volume of a coil as a function of the solution concentration $V_h(c)$. Here we neglect the eventual small differences in the concentration dependence of the expansion factor of the radius of gyration α_s of the chain ends α_h and the viscosity α_η. Of course, this approach is not limited only to equations (1) and (2), but is also applicable in any other theoretical treatments of the concentration effect on macromolecular dimensions[1,4,5,22]. By using the Eizner and Yamakawa relations, we obtain for the hydrodynamic volume:

$$V_h(c) = V_h(0)\,(1 - A_2MF_Ec - \cdots)^3 \qquad (7)$$

and:

$$V_h(c) = V_h(0)\exp(-3A_2MF_Yc) \qquad (8)$$

The next step in this theoretical model is the conversion of the changes in hydrodynamic volume according to equations (7) and (8) to variations in the elution volume V_e in g.p.c. A so-called universal calibration[25], i.e. a plot of $\log M[\eta]$ against V_e, is used in g.p.c. for expressing the dependence of V_e on the size of solute molecules. The calibration should not depend on either the nature of solute or eluent after suitable correction[26] for secondary separation effects (adsorption on gel, partition, etc.). As follows from equation (4), this universal calibration can be expressed as a plot of $\log V_h$ *versus* V_e[18,19]. The universal calibration curves established at different concentrations c coincide in this representation. The shape of the universal calibration curve is determined mainly by the geometry of the column packing, character of the gel, and distribution of pore dimensions. For semi-logarithmic ordinates in the central region of the effective separation, $\log V_h$ usually decreases linearly with increasing V_e. For simplification, we shall consider only this segment of the universal calibration curve. Thus for the infinitely dilute solution, the following approximation holds:

$$\log V_h(0) = b_1 - b_2V_e(0) \qquad (9)$$

and for a polymer solution with concentration c:

$$\log V_h(c) = b_1 - b_2V_e(c) \qquad (10)$$

Neither V_h nor elution volume at infinite dilution is measurable experimentally and is determined only by extrapolation to $c \to 0$[12–17]. The last two equations will give:

$$V_e(c) = V_e(0) + (1/b_2)\log[V_h(0)/V_h(c)] \qquad (11)$$

or

$$V_e(c) = V_e(0)\,[\log V_h(c) - b_1]/[\log V_h(0) - b_1] \qquad (12)$$

By substituting equations (7) and (8) into, for example, equation (11), we obtain relations enabling theoretical prediction of the concentration effect in g.p.c. The use of the Eizner relation for the concentration compression of coils (7), if we restrict it to the first two terms of the series, yields:

$$V_e(c) = V_e(0) - (3/b_2)\log(1 - A_2MF_Ec) \qquad (13)$$

and substitution in the Yamakawa relation (8) gives:

$$V_e(c) = V_e(0) + 1.303\,A_2MF_Yc/b_2 \qquad (14)$$

These relations show that the concentration effect in g.p.c. for the polymer solute–eluent system depends on

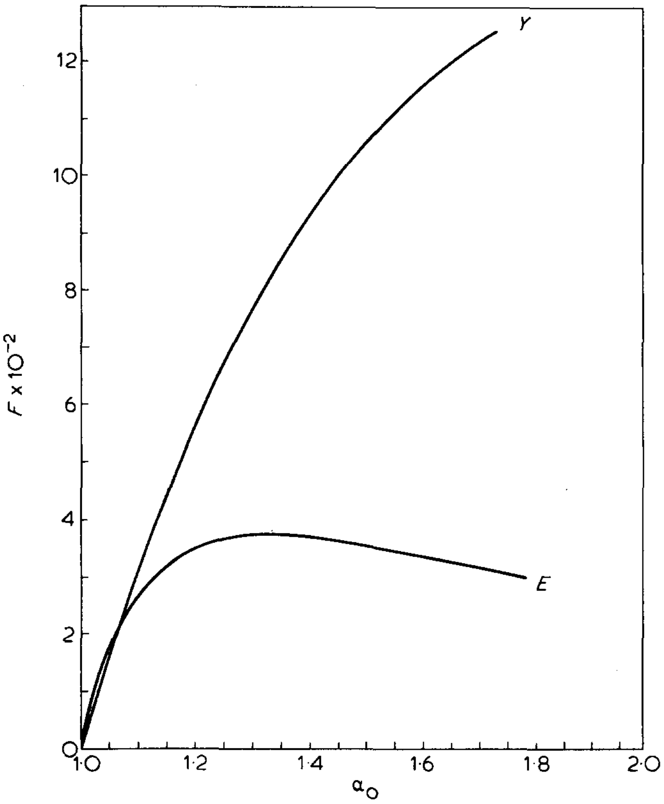

Figure 1 Plot of excluded volume functions F_E and F_Y from equations (1) and (2) as a function of expansion coefficient α_0

the second virial coefficient A_2, the solute molecular mass M and its concentration in the eluent, and the functions F_E and F_Y dependent on parameters of the excluded volume (expressed by α_0 or z). Both expressions indirectly depend on the slope of the linear part of the universal calibration, b_2, defining the selectivity of the separation in a column. The less steep the universal calibration, i.e. the higher the selectivity of the chromatographic system, the greater is the concentration effect in g.p.c. Substitution of equations (7) and (8) into equation (12) leads to analogous relations, where the intercept b_1 of the linear part of the calibration curve will serve as a parameter. For the systems where A_2 assumes a positive value, equations (13) and (14) predict a rise in the elution volume with increasing concentration in agreement, with experiment[12–17]. If, on the basis of the last two relations, the slope of the concentration dependence of V_e, $k_{th} = \mathrm{d}V_e/\mathrm{d}c$ is expressed, we obtain:

$$k_{th}^E = 1.303 A_2 M F_E / [b_2(1 - A_2 M F_E c)] \qquad (15)$$

and:

$$k_{th}^Y = 1.303 A_2 M F_Y / b_2 \qquad (16)$$

The Yamakawa expression yields a concentration-independent slope, while the Eizner relation leads to a slope indirectly dependent on concentration. However, in the region of low c, both expressions predict the slope of the concentration dependence of V_e to be directly proportional to the product A_2M as recently found[16] by the analysis of experimental results. Thus, the model qualitatively describes all substantial features of the concentration effect in g.p.c. In the following, the model is used for detailed quantitative evaluation of the concentration effects in two different polymer–eluent systems.

Concentration effect of polystyrene in tetrahydrofuran and toluene

Equations (13) and (14) were employed for calculating the plot of V_e against c for polystyrene (PS) with M between 5.1×10^4 and 1.2×10^6 in tetrahydrofuran (THF) and toluene. For estimating the values of A_2 over the whole range of molecular weights for both solvents, results of light-scattering measurements[27] were used. The results fit the empirical equation $A_2 = \mathrm{d}M^{-\mu}$ well; μ was found to be 0.30 for THF and 0.27 for toluene. *Figure 1* shows the functions F_E and F_Y dependent on the expansion factor α_0. The values of α_0 were obtained from viscometric data taking a = 0.70 and $K = 14.1 \times 10^{-3}$ cm^3 g^{-1} for THF[25] and $a = 0.73$ and $K = 9.77 \times 10^{-3}$ cm^3 g^{-1} for toluene. For K of PS in theta solvent, $K_\theta = 9.72 \times 10^{-2}$ cm^3 g^{-1} was chosen[22]. Since the theoretical plots of V_e *versus* c are compared with the experimental ones found in our laboratory for THF[16,21] and toluene[29], we used $b_2 = 0.068$ characterizing the universal calibration of log V_h *versus* V_e for a two-column system filled with inorganic gel Porasil D and E employed in the mentioned papers. *Figures 2* and *3* illustrate the extent of the coil shrinkage with increasing concentration according to equations (1) and (2) for PS in THF. Both theories show that the expansion factor, especially at higher molecular mass, rapidly decreases with polymer concentration, the decrease being steeper in the case of Yamakawa theory. An analogous course show the curves $\alpha_c = \alpha_c(c)$ for

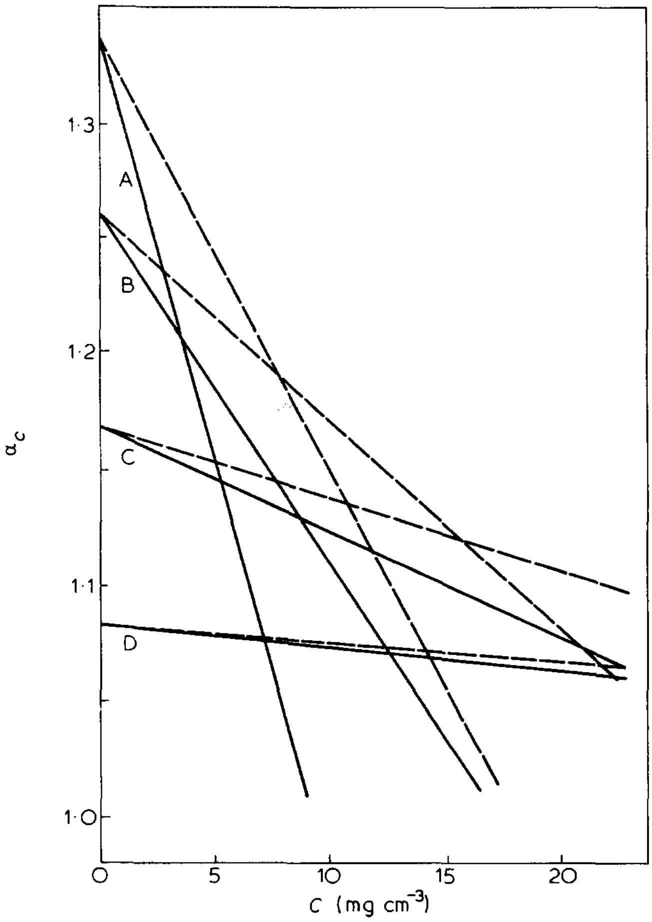

Figure 2 Variation of expansion coefficient α_c with concentration according to Eizner[2], equation (1), — — — —; and Yamakawa[3], equation (2), ———, for PS–THF. Values of M: A, 1.2×10^6; B, 4.98×10^5; C, 1.6×10^5; D, 5.1×10^4

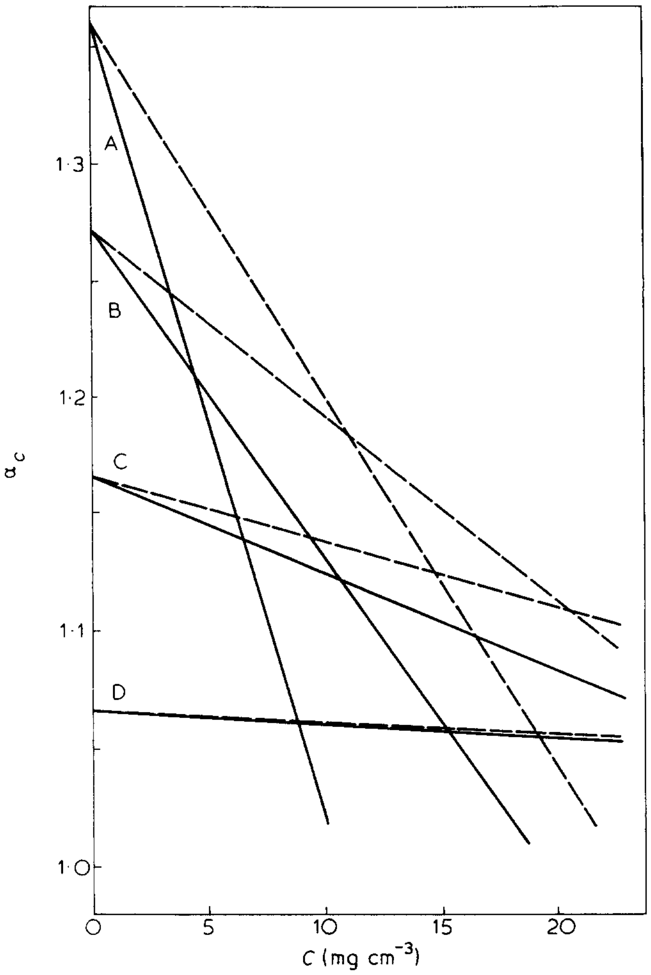

Figure 3 Variation of expansion coefficient α_c with concentration according to Eizner[2], equation (1), — — — —; and Yamakawa[3], equation (2), ———, for PS–toluene. M: A, 1.2×10^6; B, 4.98×10^5; C, 1.6×10^5; D, 5.1×10^4

PS in toluene and also the concentration dependences of the hydrodynamic volume according to equations (7) and (8).

The dependence of V_e on polymer concentration calculated according to equations (13) and (14), together with the experimentally found curves, are plotted for both solvents in *Figures 4* and *5*. For the sake of simplicity in constructing the experimental curves, the concentration of solution injected into the column c_{inj} was considered as the polymer concentration c. As is seen in *Figures 4* and *5*, both experimental and theoretical dependences are linear in the range of low c. A comparison of the curves in *Figures 4* and *5* also shows that both theoretical relations predict smaller concentration dependence of V_e than is observed. The lines calculated from equation (14) based on the Yamakawa relation are slightly steeper compared with those from the Eizner theory. This is also in accord with the fact that the decrease in the expansion factor α_0 in *Figures 2* and *3* with concentration is steeper in the Yamakawa theory. The comparison of experiments with theories (*Figures 4* and *5*) is of interest only to M about 6.7×10^5, since, for higher M, the experimental plots are affected by the considerably smaller separation ability of the gels used in papers[16,21,29]. The comparison of the experimental and theoretical slopes k_{exp} and k_{th} as a function of M is seen in *Figure 6*. Both equations (15) and (16) qualitatively correctly predict the dependence of the slope of the concentration effect on M. *Figure 7* illustrates this result still better; here, the theoretical slopes k_{th} calculated from equations (15) and (16) are plotted for both solvents as a function of the product A_2M. The experimental curve drawn in this figure was obtained by measurements of the concentration effect of PS in ten eluents of different thermodynamic quality including THF[16]. A comparison of the curves in *Figure 7* shows that both theories qualitatively correctly describe also the dependence of the slope on thermodynamic quality of eluent expressed by the value of A_2.

DISCUSSION

Comparison of experimental and theoretical concentration dependences of V_e for PS in THF and in toluene showed

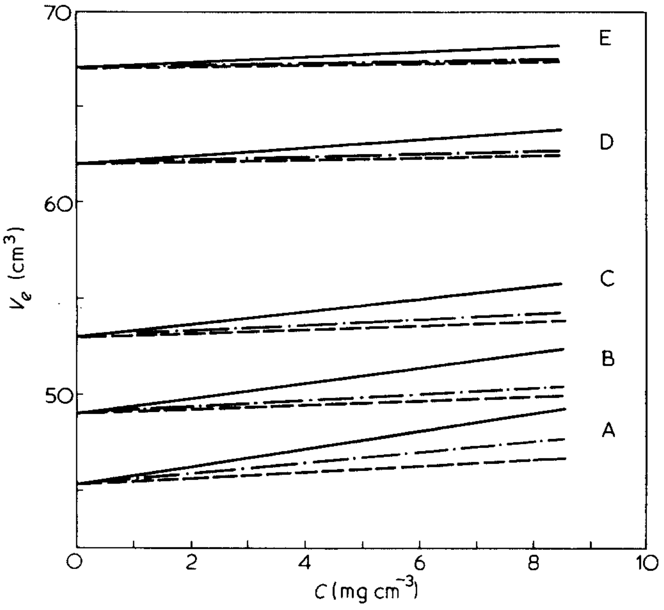

Figure 4 Concentration dependences of elution volume for PS–THF, ———, experimental data[16,21]; — — — —, calculated from equation (13); — · — · — · —, calculated from equation (14). M: A, 4.98×10^5; B, 3.2×10^5; C, 2.5×10^5; D, 9.72×10^4; E, 5.1×10^4

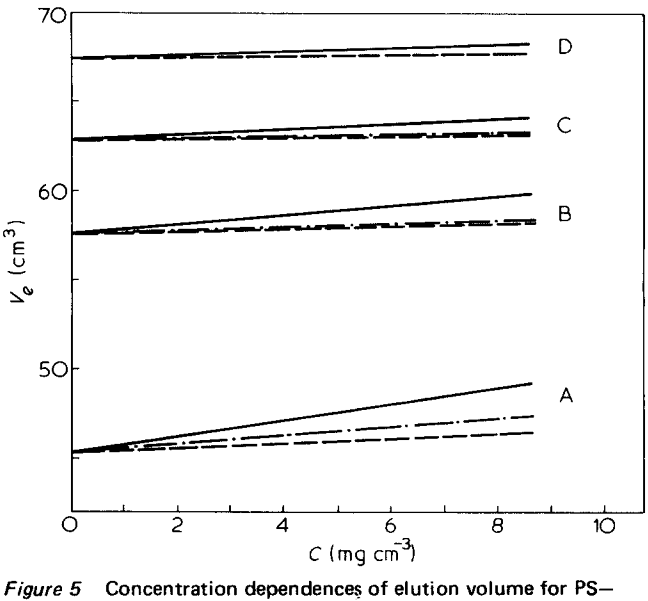

Figure 5 Concentration dependences of elution volume for PS–toluene. ———, experimental data[16,21]; — — — —, calculated from equation (13); — · — · — · —, calculated from equation (14). M: A, 4.98×10^5; B, 3.2×10^5; C, 9.72×10^4; D, 5.1×10^4

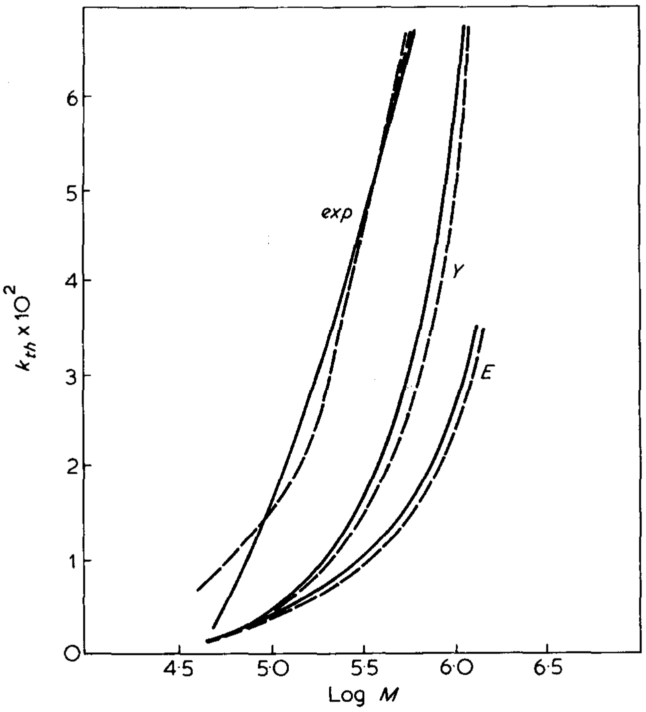

Figure 6 Plots of experimental and theoretical slopes k_{exp} and k_{th} against molecular mass. ———, PS–THF; — — — —, PS–toluene; E, calculated from equation (15); Y, calculated from equation (16)

that the proposed model of the concentration effect predicts qualitatively correct experimental results.

The agreement between theory and experiment is much better if the Yamakawa equation (2) is used, compared with the Eizner expression (1). If equation (2) is extended to power series and the first two terms of this series are compared with equation (1), it is seen that, provided $F_E = F_Y$, both expressions are practically identical over the range of low concentrations. However, the analytical functions of the excluded volume are for each theory different, although in both cases expressed by the expansion factor α_0. As it follows from the course of the functions F_E and F_Y in *Figure 1* for thermodynamically poor solvents, where the expansion factor differs slightly from unity, prediction of concentration dependence according to both relations only slightly differs. However, for thermodynamically good solvents, F_Y is much greater than F_E. Thus, a decrease in macromolecular dimensions predicted by relation (2) is substantially steeper than that according to (1) as demonstrated by a plot of α_c versus c in *Figures 2* and *3* for PS in THF and toluene. With increasing concentration, the reduction of the expansion coefficient according to *Figures 2* and *3* is approximately linear. For higher molecular masses (about 10^6 and higher), the validity of both theories is restricted only to a very narrow region of dilute solutions, since, even for small c, the calculated values of α_c assume unreal values smaller than unity. Since expression (2) predicts greater coil shrinkage with concentration, its use in our model leads to more marked changes of the elution volume V_e with concentration than the use of relation (1) (*Figures 4* and *5*).

On the other hand, after reversing the whole procedure, the comparison with the experimental curves would indicate that the Yamakawa relation describes better the coil shrinkage in the range of very dilute solution than the expression used by Eizner. Concentration plots obtained by g.p.c. might thus serve as a method of mutual comparison of the reliability of individual theoretical expression for the polymer coil shrinkage over the range of very dilute solutions. Although this method might seem to be rough, it can be improved; its significance lies in the fact that there is only a small number of alternative procedure suitable for this purpose.

The reasons for differences between the predicted and measured concentration dependences of V_e, as is seen in *Figures 4* and *5*, have to be sought not only in the reliability of theoretical relations for coil shrinkage. The theoretical model described contains several simplifications, e.g. approximation of the shape of a polymer coil by effective hydrodynamic sphere. It is implicitly assumed that relations from equilibrium thermodynamics of dilute polymer solutions can be applied to hydrodynamic processes taking place in a chromatographic column. Analogously to Rudin[18,19], we assume steric exclusion to be the only factor contributing to the concentration effect. Other secondary separation mechanisms[16,26], e.g. adsorption on gel, solute partition, are not considered. One cannot eliminate the possibility that these factors, the viscosity[30] of the eluted sample solution in interestitial volume in a column, and osmotic effects[31] contribute to disagreement between experimental and calculated curves. Underestimation of the concentration effect in calculation according to equations (13) and (14) in *Figures 4* and *5* becomes more marked when we realize that the sample concentration in the solution injected at the top of the column was taken as c for the plots of experimental curves in *Figures 4* and *5*. The difference between the injected concentration and that at the outlet of the column can be significant especially for polymers having high molecular mass[32] and large polymolecularity. Finally, the factor participating in the disagreement between experiment and theory could be the scarcity of sufficiently reliable values of virial coefficients, A_2, for the region of molecular weights studied.

Figure 8 shows the relation between the calculated and measured slopes of concentration dependence k_{th} and k_{exp} for PS in both eluents. The values of k_{th} assume only about 30% of the k_{exp} over the whole molecular mass region if

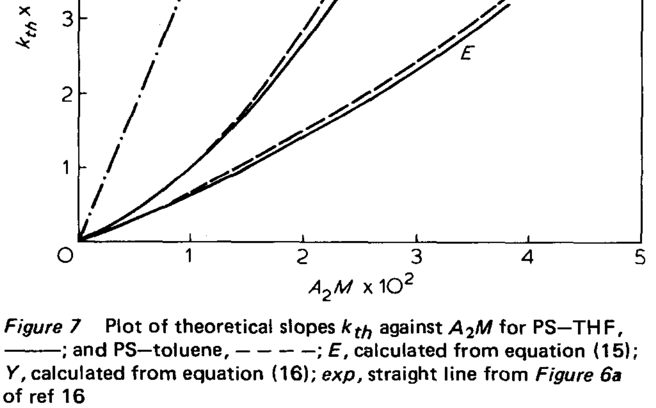

Figure 7 Plot of theoretical slopes k_{th} against A_2M for PS–THF, ———; and PS–toluene, — — — —; E, calculated from equation (15); Y, calculated from equation (16); *exp*, straight line from *Figure 6a* of ref 16

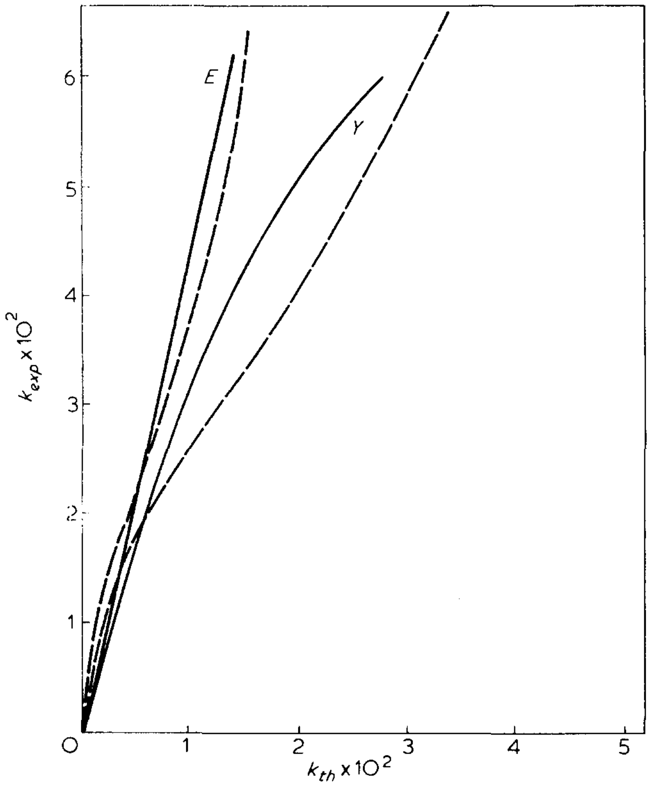

Figure 8 Mutual relations of experimental and theoretical slope, k_{exp} and k_{th}, for PS–THF, ———; and PS–toluene, – – – –. E, k_{th} calculated using equation (15); Y, k_{th} calculated using equation (16)

the Eizner relation is used, while it is about 50% for the Yamakawa relation in the domain of higher k. One of the methods for improving the agreement between theory and experiment is the semi-empirical arrangement of theoretical relations (15) and (16) by fitting to the experimental data. The fitting might be interpreted e.g. as replacement of the functions F_Y and F_E (their exact analytical form is probably the weakest point in both theories) by 'experimentally' determined function F obtained from the F_E and F_Y functions by multiplying by the correction functions f_E or f_Y. Thus, for example, a constant value of about 3.3 would follow from *Figure 8* for f_E. A more detailed description requires accumulation of more data on k_{exp} and k_{th} for various systems. This fitting procedure may be regarded in an extreme consideration as an 'improvement' of the theoretical relations (1) and (2) of the $\alpha = \alpha(c)$ and $V = V(c)$ type or, more precisely, as an approach which effectively involves all other influences on the concentration effect and compensates the shortcomings of the theoretical model. The fitting procedure is necessary also for prediction of k_{th} for systems where no universal calibration and thus neither constant b_2 were determined. Then the ratio F_Y/b_2 from equation (16) and a similar ratio for infinite dilution from equation (15) should be established by comparison with k_{exp} in one set of experiments and used for prediction in other sets.

The condition for the theory to account also for the dependence of the concentration effect on the thermodynamic quality of eluent is of the same importance as the ability to predict the plot of V_e *versus* c. Since our recent analysis of experimental data has shown[16] that the slopes of the concentration dependences of V_e correlate with the product A_2M, this aspect has been considered of primary significance for the formation of the model. The analytical form of equations (15) and (16) and the plot of theoretical slopes of k_{th} in *Figure 7* for PS in THF and in toluene justifies our previous proposal[16] for the determination of the second virial coefficient A_2 from g.p.c. measurements. *Figure 7* also shows the variation of experimental slopes with A_2M as an average value from the data obtained for PS in 10 eluents of various thermodynamic quality. Consideration of the above-mentioned relation between k_{th} and k_{exp} (*Figure 8*) suggests that, as the theoretical slopes depend on the type of solvent (through functions F_E or F_Y), so a similar dependence should also exist for the plot of k_{exp} versus A_2M. This, together with uncertainty in determination of the values of k_{exp} and in the estimate of A_2 might also explain a considerable scatter of data in the plot in *Figure 6* from ref 16. Equations (15) and (16) then show that, in theta eluents when $A_2 = 0$, elution volume is concentration independent as has been found at the very beginning of the study of the concentration effect[16,17] This observation actually stimulated detailed experimental and theoretical analysis of solvent effect on the dependence of V_e on c. But the original Rudin model[18] has not predicted the solvent effect, and its improved version[19] only takes it into account semi-empirically.

Determination of the second virial coefficient A_2 by g.p.c. measurements necessitates finding of a relation between k_{exp} and k_{th} similar to that shown in *Figure 8*. In the case of their mutual linear dependence, fitting in only one point with known values M and A_2 is sufficient for a rapid estimation of A_2 of other samples with different M. This procedure can again be regarded as a semi-empirical modification of equations (15) and (16), which is even more feasible when we realize that the factors supposedly contributing to the concentration effect in g.p.c. and not considered in the present model (e.g. viscosity) should not be appreciably affected by eluent type. In other words, the change in thermodynamic quality of the eluent influence only the extent of changes in coil dimensions with concentration. In following papers, we intend to examine in more detail how the relation between k_{th} and k_{exp} will be affected by the porosity and surface treatment of inorganic gel and the extent of its separation region, type of separated polymer and its polydispersity, and other factors.

During the preparation of the present manuscript, a paper of Mahabadi and Rudin[33] was published where they also used the Yamakawa relation (equation (2)) for explanation of concentration dependence of V_h and V_e with similar results as in the present work.

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