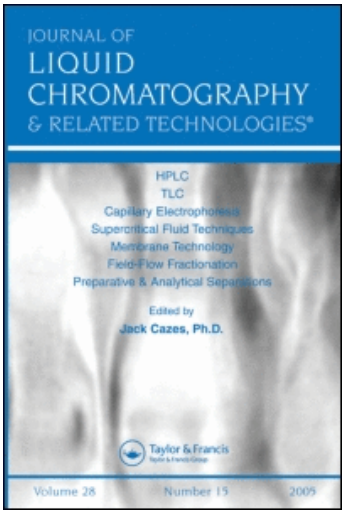

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CONCENTRATION EFFECTS IN SEC FOR POLYMER/POLYMER/SOLVENT SYSTEMS

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ABSTRACT

A model quantitatively describing the experimental shifts in elution volumes of polymeric solute A in the presence of another polymer B is developed. The concentration-dependent shrinkage of A coils has been evaluated from the intrinsic viscosity displayed by polymer A in the ternary solution formed by itself at c_A concentration + polymer B at c_B concentration + solvent. Resulting concentration effects depend on both polymer concentrations (c_A and c_B), on the intrinsic viscosities of both polymers in the solvent ($|\eta|_A$ and $|\eta|_B$), on the Huggins' coefficients k_A and k_B, and on the quadratic concentration coefficients in the polynomial expansion of η_{sp}/c, namely k'_A and k'_B. Predicted elution volumes are compared with experimental ones for two different types of literature systems: those studying polymer A elution at diverse c_A concentrations in eluents consisting of mixtures of polymer B + solvent and those in which polymer A + polymer B mixtures are injected at once in the pure solvent used as eluent. In order to eliminate experimental uncertainties about k_i and k'_i (i=A,B) values, applied k'_i values were those obtained from the empirical correlation $k'_i + 0.122 = k^2_i$ whereas k_i ones were obtained from Imai's equation.

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INTRODUCTION

To this date, the so-called "concentration effects" in steric exclusion liquid chromatography (SEC) of polymers is experimentally well established (1-5) and several theoretical models (6-11) have been proposed for its prediction. A new model accounting for concentration effects in SEC was recently developed (12), and a good agreement between experimental peak elution volumes and predicted ones was evidenced for several tested polymer/eluent/gel systems. However, several comments on all the proposed models should be underlined. The concentration range of models (6-12) applicability is not clearly defined; so, for very low concentration of solute injection, the predictability of elution volumes shown by all models is quantitatively correct; but at moderately diluted concentration of solute injection, deviations arise between experimental and predicted elution volumes. The limit between both regimes of concentration is not well established. On the other hand, several works (13-16) describing the experimental shifts in the peak elution volumes of a polymeric solute eluted in presence of another polymer have been considered to be manifestations of concentration effects, and an attempt of theoretical prediction has only been reported (15) by the Rudin's model.

This paper is dedicated to the development of a model for the prediction of elution volumes at finite concentration for a polymeric solute A in the presence of another polymer B similar or dissimilar in chemical nature to the former, and to clarify the concentration range in which the model is valid.

In SEC the commonly used magnitude for defining the size of a polymer molecule, as defined by its equivalent hydrodynamic sphere, is the hydrodynamic volume ($M[\eta]$), but it is well known that the size of a macromolecular coil in solution depends upon its concentration (17). In this model, it is assumed that coil shrinkage is due to the joint contribution of thermodynamic and hydrodynamic binary and ternary interactions between A and B polymers in the presence of a good common solvent. Both contributions are introduced in our model through the coefficients of the linear (Huggins' coefficients,

k_A and k_B) and quadratic (k'_A and k'_B) concentrations terms in the polynomial expansion of η_{sp}/c (18).

As test systems, the following ones with reported data on elution volumes have been studied: diverse solutions of polystyrene (PS) or poly(methyl methacrylate) (PMMA) in (THF + PS) as eluent (13,14), mixtures of two PSs in THF (15), mixtures of PS + PMMA in THF (15) and mixtures of PS + polybutadiene (PBD) in THF (16).

THEORY

The developed formalism, used to estimate the hydrodynamic volumes at infinite dilution and finite concentration (12,19), is based on the viscometric concepts on polymer A/polymer B/solvent ternary systems. There are two ways to construct the above ternary system: a mixture of polymer A and polymer B is dissolved in the solvent, or the polymer A is dissolved in a dilute solution of solvent + polymer B. The universal calibration equation for the polymer A, at infinite dilution, in the presence of B, is given by

$$\log M|\eta|_{A,c_B} = Q - PV_e(0) \qquad (1)$$

where Q and P are calibration constants, $V_e(0)$ is the elution volume at infinite dilution of A in presence of polymer B at a finite concentration, c_B, and $|\eta|_{A,c_B}$ is the intrinsic viscosity of polymer A in a solution at c_B of polymer B in the solvent. $V_e(0)$ cannot be directly evaluated and must be found by extrapolation. The universal calibration for polymer A at finite concentrations of both A and B polymers (13) is given by

$$\log M|\eta|_{A,c_A+c_B} = Q - PV_e(c_A) \qquad (2)$$

where now $V_e(c_A)$ is the elution volume of polymer A injected at the finite concentration c_A and $|\eta|_{A,c_A+c_B}$ is the intrinsic viscosity displayed by polymer A in a ternary system consisting of solvent, polymer A at c_A and polymer B at c_B. The subtraction of eqs.(1) and (2) yields for $V_e(c_A)$:

$$V_e(c_A) = V_e(0) - \frac{1}{P} \log \frac{|\eta|_{A,c_A+c_B}}{|\eta|_{A,c_B}} \qquad (3)$$

Since $|\eta|_{A,c_A+c_B}$ and $|\eta|_{A,c_B}$ are not usually available experimental magnitudes, the direct applicability of eq.(3) remains limited and it must be transformed into a new one given in terms of available experimental magnitudes, such as $|\eta|_A$ and $|\eta|_B$. That transformation can be done recalling $|\eta|_{A,c_A+c_B}$ and $|\eta|_{A,c_B}$ definitions:

$$|\eta|_{A,c_A+c_B}=\lim_{c_A'\to 0}\frac{(t_{c_A'+c_A+c_B}/t_{c_A+c_B})-1}{c_A'};\quad |\eta|_{A,c_B}=\lim_{c_A'\to 0}\frac{(t_{c_A'+c_B}/t_{c_B})-1}{c_A'} \qquad (4)$$

where $t_{c_A'+c_A+c_B}$ is the flow time through a capillary of a solution of polymer A at c_A' concentration in the "solvent" with flow time $t_{c_A+c_B}$ formed by polymer A at c_A concentration + polymer B at c_B concentration in the pure solvent. $t_{c_A'+c_B}$ stands for the flow time of a solution of polymer A at c_A' concentration in the "solvent" with flow time t_{c_B} formed by polymer B at c_B concentration in the pure solvent. The evaluation of all the above flow times can be done through the Krigbaum and Wall (20) and Cragg and Bigelow (21) formalisms for multicomponent systems. According to these formalisms the specific viscosity of a solution of a mixture of polymers at c_m concentration is given by

$$\frac{\eta_{sp,m}}{c_m}=|\eta|_m+b_m c_m+b_m' c_m^2+\cdots$$

where $|\eta|_m$ stands for the intrinsic viscosity of the mixed polymer, and b_m, b_m', ... for the viscometric interaction parameters of the mixed polymer. Taking as an example the solution of polymer A at c_A' concentration and polymer B at c_B concentration ($c_m = c_A' + c_B$), recalling η_{sp} definition, the above eq. can be written as

$$\frac{\eta_{sp,m}}{c_m}=|\eta|_m+b_m c_m+b_m' c_m^2+\cdots=\frac{(t_{c_A'+c_B}/t_0)-1}{c_A'+c_B}$$

which is transformed into (20,21)

$$|\eta|_A w_A+|\eta|_B w_B+(b_A^{1/2}w_A+b_B^{1/2}w_B)^2(c_A'+c_B)+$$
$$(b_A'^{1/3}w_A+b_B'^{1/3}w_B)^3(c_A'+c_B)^2+\cdots=\frac{(t_{c_A'+c_B}/t_0)-1}{c_A'+c_B} \qquad (5)$$

This eq. yields $t_{c_A'+c_B}$ in terms of the corresponding intrinsic

viscosities and viscometric interaction parameters of the individual polymers. Changing from mass fraction to concentration, $w_i=c_i/(c'_A+c_B)$, eq.(5) yields

$$\frac{(t_{c'_A+c_B}/t_0)-1}{c'_A+c_B} = |\eta|_A \frac{c'_A}{c'_A+c_B} + |\eta|_B \frac{c_B}{c'_A+c_B} + (b_A^{1/2}\frac{c'_A}{c'_A+c_B} + b_B^{1/2}\frac{c_B}{c'_A+c_B})^2 (c'_A+c_B) + (b'^{1/3}_A \frac{c'_A}{c'_A+c_B} + b'^{1/3}_B \frac{c_B}{c'_A+c_B})^3 (c'_A+c_B)^2 + \cdots \quad (6)$$

By expanding the second and third powers and recalling (20,21) for short that $b_{AB}=(b_A b_B)^{1/2}$; $b'_{AAB}=(b'_A b'_A b'_B)^{1/3}$ and $b'_{BBA}=(b'_B b'_B b'_A)^{1/3}$, eq.(6) is finally transformed into

$$t_{c'_A+c_B} = t_0\,[1+|\eta|_A c'_A+|\eta|_B c_B+b_A c'^2_A+b_B c^2_B+2b_{AB}c'_A c_B+b'_A c'^3_A+b'_B c^3_B+3b'_{AAB}c'^2_A c_B+3b'_{BBA}c'_A c^2_B+\cdots \quad (7)$$

The remaining flow times can be evaluated in a similar way, for instance changing c'_A by c'_A+c_A in order to get $t_{c'_A+c_A+c_B}$, or c'_A by c_A to get $t_{c_A+c_B}$, or making $c'_A=0$ when intending to obtain t_{c_B}. The obtained eqs. are

$$t_{c'_A+c_A+c_B} = t_0\,[1+|\eta|_A(c'_A+c_A)+|\eta|_B c_B+b_A(c'_A+c_A)^2+\cdots \quad (8a)$$

$$t_{c_A+c_B} = t_0\,[1+|\eta|_A c_A+|\eta|_B c_B+b_A c^2_A+\cdots \quad (8b)$$

$$t_{c_B} = t_0\,[1+|\eta|_B c_B+b_B c^2_B+b'_B c^3_B+\cdots \quad (8c)$$

The appropriate substitution of the above flow times in eqs. (4) yields

$$|\eta|_{A,c_A+c_B} = (|\eta|_A+2b_A c_A+2b_{AB}c_B+3b'_A c^2_A+3b'_{BBA}c^2_B+6b'_{AAB}c_A c_B)/(1+|\eta|_A c_A+|\eta|_B c_B+b_A c^2_A+b_B c^2_B+2b_{AB}c_A c_B+b'_A c^3_A+b'_B c^3_B+3b'_{AAB}c^2_A c_B+3b'_{BBA}c_A c^2_B) \quad (9)$$

$$|\eta|_{A,c_B} = \frac{|\eta|_A+2b_{AB}c_B+3b'_{BBA}c^2_B}{1+|\eta|_B c_B+b_B c^2_B+b'_B c^3_B} \quad (10)$$

Eq.(10) has been widely used (22,23) without the b' terms.

The substitution of $|\eta|_{A,c_A+c_B}$ and $|\eta|_{A,c_B}$ from eqs.(9) and (10) and the introduction of $k_i=b_i|\eta|_i^{-2}$ and $k'_i=b'_i|\eta|_i^{-3}$ in eq.(3) yields

$$V_e(c_A) = V_e(0) - \frac{1}{P}\log$$

$$\left[\frac{1+|\eta|_B c_B+(k_B^{1/2}|\eta|_B c_B)^2+(k_B'^{1/3}|\eta|_B c_B)^3}{1+|\eta|_A c_A+|\eta|_B c_B+(k_A^{1/2}|\eta|_A c_A+k_B^{1/2}|\eta|_B c_B)^2+(k_A'^{1/3}|\eta|_A c_A+k_B'^{1/3}|\eta|_B c_B)^3}\right.$$

$$\left.\frac{1+2k_A^{1/2}(k_A^{1/2}|\eta|_A c_A+k_B^{1/2}|\eta|_B c_B)+3k_A'^{1/3}(k_A'^{1/3}|\eta|_A c_A+k_B'^{1/3}|\eta|_B c_B)^2}{1+2k_A^{1/2}k_B^{1/2}|\eta|_B c_B+3k_A'^{1/3}k_B'^{2/3}|\eta|_B^2 c_B^2}\right] \quad (11)$$

Defining the new variables $\alpha \equiv k_A^{1/2}|\eta|_A c_A + k_B^{1/2}|\eta|_B c_B$ and $\beta \equiv k_A'^{1/3}|\eta|_A c_A + k_B'^{1/3}|\eta|_B c_B$, eq.(11) is finally rearranged into

$$V_e(c_A) = V_e(0) - \frac{1}{P}\log\prod_{m=1}^{2}\left[\frac{1+2k_A^{1/2}\alpha+3k_A'^{1/3}\beta^2}{1+|\eta|_A c_A+|\eta|_B c_B+\alpha^2+\beta^3}\right]^{3-2m}_{m=2;c_A=0} \quad (12)$$

The above equation is of general aplication; it predicts the shifts in elution volumes due to concentration effects of a polymer A in the absence or presence of another polymer B (similar or dissimilar in chemical nature to A).

RESULTS AND DISCUSSION

Prior to testing the validity of eq.(12), some considerations on its potential applicability should be remarked upon. The direct application of eq.(12) demands the knowledge of k_i and k_i' magnitudes, not easily available to chromatographists and of which accurate experimental determinations are not easy tasks. In order to overcome these dificulties the following alternative is offered.

According to Imai (24), Huggins' coefficients, k_i, are related to viscometric expansion factors, α_η, through the equation

$$k_i = k_{i,\theta}\,\alpha_\eta^{-4} + C(1 - \alpha_\eta^{-2}) \quad (13)$$

where $k_{i,\theta}$, the Huggins' coefficient at θ-conditions and the C coefficient are independent of temperature, solvent power and molar mass (25), with the most commonly accepted values $k_{i,\theta} = 0.5$

and C = 0.3 (26). Recalling α_η definition, $\alpha_\eta^3 = |\eta|_i / |\eta|_{i,\theta}$ with $|\eta|_{i,\theta} = K_{i,\theta} M_i^{1/2}$, eq.(13) is transformed into

$$k_i = 0.5\left[K_{i,\theta}^{4/3}\, M_i^{2/3}\, |\eta|_i^{-4/3}\right] + 0.3\left[1-(K_{i,\theta}^{2/3}\, M_i^{1/3}|\eta|_i^{-2/3})\right] \quad (14)$$

which yields k_i in terms of the more accesible K_θ and $|\eta|_i$ magnitudes. Similarly, k_i' substitution in eq.(12) by other more accesible magnitudes, can be done through the correlation $(k_i' + C')/k_i^2 = 1$ valid for polymers coils (27). Diverse C' values have been suggested: 0.125 (28), 0.09 (29), 0.08 (30) and 0.122(31). This last value, recently proposed, has been evaluated from experimental data for PMMA (32) in p-dioxane and 1,2-dichloroethane at 20°C and it is the one adopted in this paper. Therefore,

$$(k_i' + 0.122) = k_i^2 \quad (15)$$

Reported data on experimental elution volumes of a polymeric solute A (taken as reference) eluted in presence of another polymer B,are scarce. The systems so far tested in this paper are listed in table 1. Runs 1 to 8 correspond to elution of diverse PS samples (at several c_A concentrations) in binary eluents (THF + diverse PS at several c_B concentrations) and the experimental results were published in a numerical way (14), consequently the predicted results are presented in the same way. The remaining experimental and predicted elution volumes are shown in a graphic form. In runs 9 to 25 different samples of PS or PMMA at several c_A concentrations eluted in binary eluents (THF + PS-43000 at four c_B concentrations) (13). Finally, runs 26 to 34 correspond to polymer A (c_A) + polymer B (c_B) mixtures injected in pure THF as eluent (15,16) with polymer A = diverse PS samples and polymer B = diverse PS or PMMA or PBD samples.

In table 2, the viscometric constants in THF for the eluted polymers are shown and in table 3 the parameters necessary for eq. (12) application. $|\eta|_A$ and $|\eta|_B$ have been evaluated through the corresponding viscometric equations from table 2. k_A and k_B have been calculated through eq.(14) with K_θ from table 2. In runs 1 to 8, P values have been obtained from the slopes of log $M|\eta|_{A,c_B}$ vs.

TABLE 1

Studied Polymer/Polymer/Solvent Systems

RUN	SAMPLE / ELUENT*	REFERENCE
1	PS-620000/PS-620000 (1.5 mg/ml) + THF	
2	PS-2280000/ " " + "	
3	PS-620000/PS-12500 (2.0 mg/ml) + THF	
4	PS-412000/ " " + "	
5	PS-2280000/PS-4000 (2.0 mg/ml) + THF	14
6	PS-2280000/ " " + "	
7	PS-620000/ " " + "	
8	PS-412000/ " " + "	
9	PS-498000/PS-43000 (10 mg/ml) + THF	
10	" / " (7.5 ") + "	
11	" / " (5.0 ") + "	
12	" / " (0.0 ") + "	
13	PS-160000/ " (10 mg/ml) + "	
14	" / " (7.5 ") + "	
15	" / " (5.0 ") + "	
16	" / " (0.0 ") + "	
17	PS-97200 / " (10 mg/ml) + "	13
18	" / " (7.5 ") + "	
19	" / " (5.0 ") + "	
20	" / " (0.0 ") + "	
21	PS-670000/ " (5.0mg/ml) + "	
22	PS-51000 / " (") + "	
23	PMMA-34800/ " (") + "	
24	PMMA-420000/ " (") + "	
25	PMMA-34800/ " (") + "	
26	PS-1800000 + PS-20400 (4 mg/ml) / THF	
27	PS-1800000 + PS-200000(") / "	
28	PS-860000 + PS-200000 (") / "	
29	PS-200000 + PS-860000 (") / "	15
30	PS-1800000+PMMA-130000(") / "	
31	PS-1800000+PBD-170000 (2 mg/ml) / "	
32	PS-390000 + PBD-170000 (0.0 mg/ml)/ THF	
33	PS-390000 + PBD-170000 (2.0 ")/ "	16
34	PS-390000 + PBD-170000 (4.0 ")/ "	

* Figures in parenthesis are for polymer concentration. The first polymer is always polymer A, the second is, of course, polymer B.

TABLE 2

Viscometric Constants in THF for the Systems Studied

POLYMERS	$K_\theta \times 10^3$ ml/g	$K \times 10^3$ ml/g	a	RUN
PS	74.5(34)	11.8(33)	0.709(33)	1-8
PS	74.5(34)	14.1(13)	0.70 (13)	9-25
PMMA	57.5(35)	10.4(36)	0.697(36)	
PS	74.5(34)	6.82(15)	0.766(15)	
PMMA	69.0(15)	12.8 (15)	0.69 (15)	26-34
PBD	166.0(15)	45.7 (15)	0.693(15)	

$V_e(0)$ plots (14). In runs 9 to 25, the same magnitude has been evaluated from the universal calibration plots given in the original reference (13). In runs 26 to 34, P values have been obtained by plotting log $M|\eta|$ vs. $V_e(0)$ data from diverse references (15,16). $V_e(0)$ values are directly reported for runs 1 to 8 in reference(14), the remaining ones have been obtained by extrapolation. Finally, k_i' values are not enclosed in table 3 because they are direct from k_i data through eq.(15).

Two different kinds of systems are studied in this paper:

a) Elution of polymer A at diverse c_A concentrations in eluent consisting of polymer B + THF, polymer A being similar or dissimilar in chemical nature to polymer B. (Runs 1 to 25, table 1).

b) Elution of polymer A + polymer B mixtures in THF as eluent, at diverse c_A concentrations and c_B constant. (Runs 26 to 34, table 1).

Regarding the first kind of systems, in table 4 experimental (14) and predicted (through eq.(12)) elution volumes for runs 1 to 8 are gathered. In these runs polymer A is always in the presence of polymer B, both into the pores and in the interstices because of the lower molecular size of polymer B. Moreover, total polymer concentration ($c_m = c_A + c_B$) anywhere in the column is always lower than 5.1 mg/ml, polymers solutions being in the dilute concentration

TABLE 3

Parameters Used for the Evaluation of Concentration Effects with eq. (12).

RUN	$\|\eta\|_A$ ml/g	$\|\eta\|_B$ ml/g	k_A	k_B	P^* ml^{-1}	$V_e(0)^*$ ml
1	185.0	185.0	0.268	0.268	0.389	27.08
2	413.1	"	0.262	"	"	24.69
3	185.0	9.475	0.268	0.446	0.290	26.04
4	150.2	"	0.269	"	"	26.83
5	413.1	"	0.262	"	0.418	24.24
6	413.1	4.224	"	0.556	0.414	23.74
7	185.0	"	0.268	"	0.258	25.89
8	150.2	"	0.269	"	"	26.81
9	137.2	24.70	0.281	0.348	0.064	48.3
10	"	"	"	"	"	48.0
11	"	"	"	"	"	47.4
12	"	—	"	—	"	46.0
13	61.96	"	0.304	"	"	62.5
14	"	"	"	"	"	62.2
15	"	"	"	"	"	61.7
16	"	—	"	—	"	60.0
17	43.71	"	0.318	"	"	67.1
18	"	"	"	"	"	66.9
19	"	"	"	"	0.065	66.3
20	"	—	"	—	0.064	65.0
21	168.84	"	0.276	"	0.065	45.0
22	27.83	"	0.341	"	"	71.7
23	105.56	"	0.286	"	"	48.9
24	86.38	"	0.292	"	"	54.4
25	15.22	"	0.376	"	"	73.3
26	422	13.64	0.258	0.436	0.068	103.8
27	"	78.41	"	0.290	"	103.0
28	240	"	0.264	"	"	111.1
29	78.41	240	0.290	0.264	0.075	125.5
30	422	43.23	0.258	0.331	0.068	103.0
31	"	192.6	"	0.275	"	104.0
32	130.8	—	0.274	—	0.086	136.7
33	"	192.6	"	0.255	"	137.6
34	"	"	"	"	"	139.8

* Units of P and $V_e(0)$ are given in $(count)^{-1}$ and (count) for 1-8 runs and in ml^{-1} and ml for the remaining runs.

TABLE 4

Comparison Between Experimental(14) and Predicted Elution Volumes with eqs.(12) and (16) for Several PSs in (THF + PS).

RUN	c_A mg/ml	V_e^{exp} count	$V_e(c_A)$ eq.(12)	$V_e(c_A)$ eq.(16)
	3.0	27.31	27.37	27.31
1	2.0	27.24	27.27	27.24
	1.2	27.19	27.20	27.18
	3.0	25.30	25.34	25.17
2	2.0	25.00	25.13	25.03
	1.0	24.90	24.91	24.87
	2.9	26.40	26.42	26.38
3	2.0	26.28	26.30	26.28
	1.2	26.20	26.20	26.19
	3.1	27.32	27.17	27.13
4	2.4	27.20	27.09	27.06
	1.0	27.00	26.95	26.93
	2.9	25.00	24.83	24.71
5	2.0	24.75	24.65	24.59
	1.2	24.50	24.49	24.46
	3.0	24.14	24.36	24.23
6	2.0	24.00	24.16	24.09
	0.9	23.83	23.93	23.91
	3.0	26.26	26.31	26.27
7	2.0	26.10	26.15	26.13
	1.0	26.00	26.02	26.02
	3.0	26.96	27.13	27.10
8	2.1	26.93	27.03	27.02
	1.1	26.87	26.93	26.92

range. In this case, second c_m and higher order powers in eq. (4) may be neglected and a simpler expression than eq. (12), can be deduced, namely

$$V_e(c_A)=V_e(0)-\frac{1}{P}\log\frac{(1+|\eta|_B c_B+k_B|\eta|_B^2 c_B^2)(1+2k_A|\eta|_A c_A+2(k_A k_B)^{1/2}|\eta|_B c_B)}{(1+|\eta|_A c_A+|\eta|_B c_B+\alpha^2)(1+2(k_A k_B)^{1/2}|\eta|_B c_B)} \tag{16}$$

in which b_i' and k_i' terms vanish. The above simplified equation has

also been applied to runs 1 to 8 and the results also are listed in table 4. As expected, negligible differences are found between predicted, both through eqs.(12) and (16), and experimental elution volumes.

In figure 1, experimental (filled points) and predicted both through the general eq.(12) (continous lines) and through the simplified eq.(16) (dashed lines) elution volumes are shown for the remaining runs 9 to 25 of the eluate (polymer A)/ eluent (polymer B = PS-43000 + THF) type. Regarding c_A values, up to $c_A \sim$ 5-6 mg/ml in the most unfavorable situations (high polymer A molecular sizes) both predicted curves are almost coincident. At c_A higher values predicted results through eq.(12) fit better to experimental ones than those evaluated from the approximate eq.(16), which, with independence of polymer B concentration in the eluent, seems to validate the b'_m introduction in eq.(4) and therefore to confirm the elution volume dependence on k'_i (i=A,B). Deviations between theoretical and experimental results start to become appreciable at c_A concentrations above 10-12 mg/ml, the former being lower than the latter. Non-exclusion effects (37), not considered so far in this model, as well as the uncertainty on $|\eta|_i$, k_i and k'_i data, are probably responsible for the observed deviations.

A last point about runs 9 to 25 deserves a brief comment. The nominated d runs in figure 1 describe concentration effects at c_B=0. Of course, eq.(12) can, in these cases, be simplified to

$$V_e(c_A)=V_e(0)-\frac{1}{P}\log\frac{1+2k_A|\eta|_A c_A+3k'_A|\eta|_A c_A^2}{1+|\eta|_A c_A+k_A|\eta|_A^2 c_A^2+k'_A|\eta|_A^3 c_A^3} \qquad (17)$$

This equation is able to predict concentration effects for a polymer A eluted in a single or mixed-solvent. Finally, considering k'_A = 0 and c_B = 0 eq.(17) can be further simplied to

$$V_e(c_A) = V_e(0)-\frac{1}{P}\log\frac{1+2k_A|\eta|_A c_A}{1+|\eta|_A c_A+k_A|\eta|_A^2 c_A^2} \qquad (18)$$

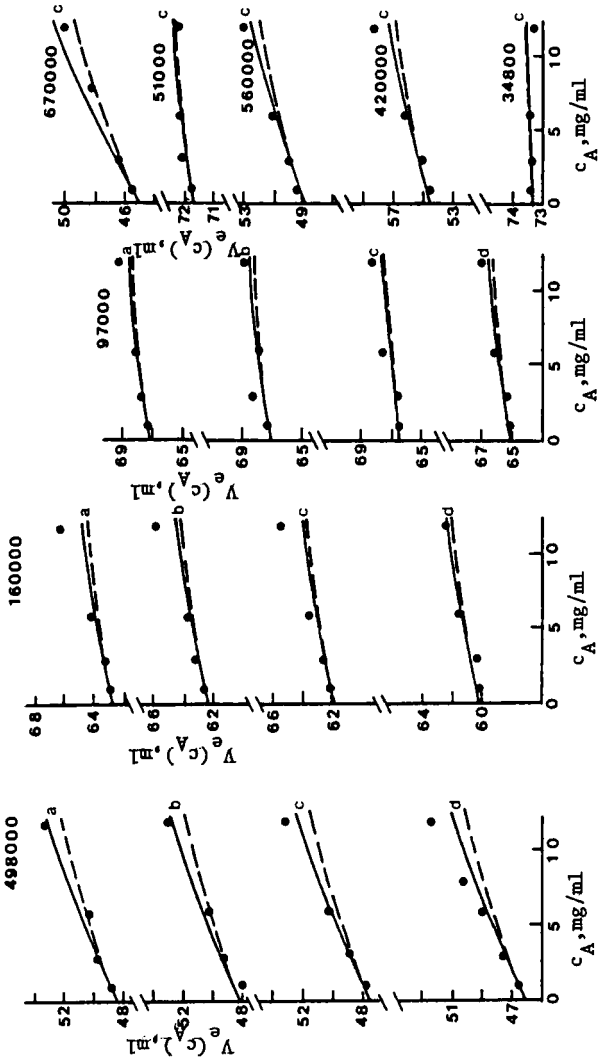

FIGURE 1. Comparison between experimental (●)(13) and calculated from eqs.(12)(——) and (16)(- - - -) elution volumes. Eluent composition: a) THF+10 mg/ml of PS-43000; b) THF+7.5 mg/ml of PS-43000; c) THF+5.0 mg/ml of PS-43000· d) pure THF.

equivalent to

$$V_e(c_A)=V_e(0) + \frac{0.4343}{P}\left[(1-2k_A)|\eta|_A c_A+(3k_A-1)|\eta|_A^2 c_A^2\right] \qquad (18')$$

its validity to predict concentration effects in dilute polymer solutions was thoroughly tested (12).

Regarding the second type of studied systems, those consisting on elution of polymer A + polymer B mixtures in THF as eluent, polymer B being similar or dissimilar in chemical nature to A (see runs 26 to 34 in table 1) both theoretical from eqs.(12) and (16) are compared with experimental elution volumes in figures 2 and 3. The predicted elution behaviour for this set of runs follows similar trends to those observed for the previous set (runs 1 to 25), therefore a parallel discussion of what has already been commented would be applicable once more, in spite of the underlying difference existing between both sets of runs. So, in the previous set of runs, polymer A is accompanied by polymer B (in the eluent) all along the column, whereas in the last runs polymer A leaves polymer B presence somewhere in the column, the sooner the difference in size is higher between A and B molecules. In fact, that difference is one more of the effects to be enclosed in the "dilution effects" chapter. Dilution effects are not taken into account by most of the models (10-12) nor are they by the present one. Leaving aside a discussion about the intrinsic validity of the diverse models, the approach of ignoring dilution effects seems to hold for all of them. Results for runs 26 to 34 are along this line, once more confirming the validity of the approach.

As a conclussion and for both types of runs (polymer B in the eluent or simultaneously injected with A) both the general eq.(12) and its simplified version eq.(16) fairly predict elution volumes up to $c_A \sim$ 5-6 mg/ml. To correctly predict elution volumes at higher c_A, up to about 10 mg/ml, k'_A values must be considered through eq. (12). Finally, at c_A above 10 mg/ml no negligible deviations between predicted by the model and experimental elution volumes start to appear, probably due to the appearence of non-exclusion effects (37).

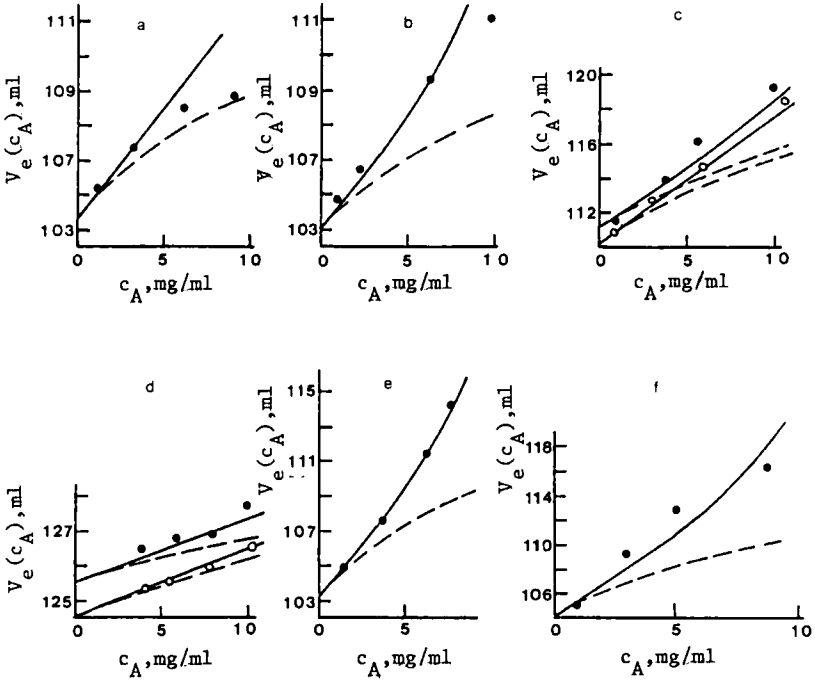

FIGURE 2. Comparison between experimental (●, ○)(15) and predicted through eqs.(12)(———) and (16)(----) elution volumes at PS diverse concentrations in THF. Injected samples: a) PS-1800000+4 mg/ml of PS-20400; b) PS-1800000+4 mg/ml of PS-200000; c) (●) PS-860000+4 mg/ml of PS-200000; (○) PS-860000 in pure THF; d) (●) PS-200000+4 mg/ml of PS-860000; (○) PS-200000 in pure THF; e) PS-1800000+4 mg/ml of PMMA-130000; f) PS-1800000+2 mg/ml of PBD.

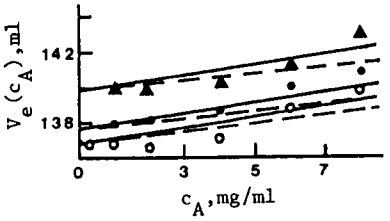

FIGURE 3. Experimental (16) and calculated through eqs. (12)(———) and (16)(----) elution volumes at diverse concentrations for PS in THF. Injected samples: (▲) PS-390000+4 mg/ml of PBD-170000; (●) PS-390000+2 mg/ml of PBD-170000; (○) PS-390000 in pure THF.

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