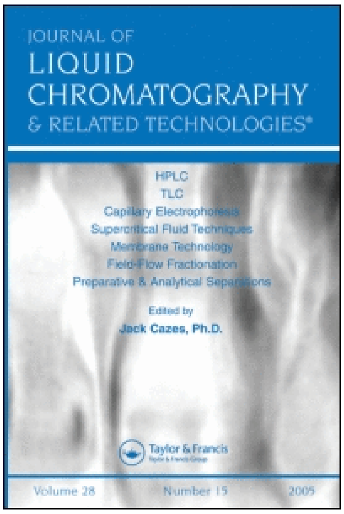

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QUANTITATIVE PREDICTION OF CONCENTRATION EFFECTS IN STERIC EXCLUSION CHROMATOGRAPHY

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ABSTRACT

A semiempirical model, based on a previous one quantitatively describing the dependence of the elution volume, $V(c_A)$, on the concentration of injected polymer, c_A, in exclusion chromatography (SEC) at dilute solutions, has been developed. In the derived equation, concentration effects are mainly governed by the Huggins' coefficient, k_A, and by the quadratic coefficient in the polynomial expansion of the reduced specific viscosity, k'_A. Because of the incertitudes on reliable k_A and k'_A values, these are respectively removed from the model through the Imai's equation and the empirical correlation $k'_A + 0.122 = k_A^2$, here obtained. Thus, predicted elution volumes besides polymer concentration only depend on the polymer intrinsic viscosity and on its unperturbed dimensions constant, K_θ. The polymer concentration range of model applicability is up to moderately diluted polymer solutions, as a comparison between predicted and experimental elution volumes for diverse literature systems shows.

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INTRODUCTION

Most of the models predicting concentration effects in steric exclusion liquid chromatography (SEC) quantify these effects through the evaluation of coil shrinkage suffered by macromolecular solutes at finite concentrations (1-3). The differences among the models are in the physical parameter selected to define the macromolecular interactions. Since the proposed models look for an easy application only first order interactions are usually accounted for and superior interaction terms neglected. As a result, and leaving aside a discussion about the intrinsic validity of the diverse reported models, predicted elution volumes only fit to experimental volumes at very diluted polymer concentration but the higher the polymer concentrations the larger the deviations between both set of data, predicted values being lower than experimental ones.

In this work, our previous model (3) is extended to be applicable at moderate polymer concentrations. The concentration dependent shrinkage of coils is evaluated from the intrinsic viscosity displayed by polymer A in the binary solution formed by itself at c_A concentration and the solvent (eluent). In the derived equation concentration effects are mainly governed by Huggins' coefficient, k_A, and by the quadratic coefficient in the polynomial expansion of η_{sp}/c, k'_A. Both coefficients account for hydrodynamic and thermodynamic interactions. Moreover, in order to eliminate experimental uncertainties on k_A and k'_A, as well as to facilitate the model applicability, k_A and k'_A are respectively removed from the derived general equation through the Imai's expression (4) and through the empirical correlation $k'_A + 0.122 = k_A^2$ (5), which is obtained and discussed in this work.

As the comparison between predicted and experimental elution volumes for diverse literature polymer/eluent/gel systems show, the model fairly describes the dependence of concentration effects both on polymer concentration and polymer molecular weight.

EXPERIMENTAL

Specific viscosities of poly(methyl methacrylate)(PMMA) in p-dioxane and 1,2-dichloroethane at 20°C, at eight concentrations ($c \simeq 0-12$ mg/ml) were measured with a conventional Ubbelohde viscometer. From plots η_{sp}/c vs. c, coefficients k and k' were evaluated according to

$$\frac{\eta_{sp}}{c} = |\eta| + k|\eta|^2 c + k'|\eta|^3 c^2 \qquad (1)$$

The studied polymers were narrow distribution fractions ($I \leq 1.2$) in the molecular weight range 15000-1500000.

THEORY

An universal calibration is usually applied in SEC in order to characterize polymers (6). The universal calibration concept assumes a linear functionallity between the log of the macromolecule hydrodynamic volume at infinite dilution in any solvent, $V_h(0)$, and the elution volume at the maximum of the chromatogram, PEV. However, at finite concentration, c_A, the macromolecule hydrodynamic volume, $V_h(c_A)$, is strongly dependent on polymer concentration (7), this dependence being more pronounced the higher molecular weight of the polymer sample (8,9). Therefore, at a given temperature, PEV will vary with the polymer molecular weight and with the concentration of injected solution. The universal calibration equation at infinite dilution is

$$\log V_h(0) = \log M|\eta|_A = Q - PV(0) \qquad (2)$$

where M and $|\eta|_A$ are molecular weight and intrinsic viscosity of the injected sample, respectively, Q and P are calibration constants and V(0) is the evaluated PEV at infinite dilution of sample injection. The universal calibration will be also hold for injected polymer solution at c_A concentration, since the eluent and other operational conditions (column packing, temperature, etc.) will remain constants (10), and it should be given by

$$\log V_h(c_A) = Q - PV(c_A) \qquad (3)$$

being $V_h(c_A)$ and $V(c_A)$ the hydrodynamic volume and the elution volume, respectively, of the polymer at c_A concentration in the solvent. In fact, the polymer A in such a solution would have an intrinsic viscosity $|\eta|_{A,c_A}$ (3). In the above equation it is assumed that the dilution of the injected solution taking place along the column is negligible, which is only valid for monodisperse samples (2).

Assuming in eq.(3) that $V_h(c_A) = M|\eta|_{A,c_A}$ (3), the substraction between eqs.(2) and (3) yields

$$-P\left[V(c_A) - V(0)\right] = \log \frac{|\eta|_{A,c_A}}{|\eta|_A} \qquad (4)$$

this equation being basic to evaluate from $|\eta|_{A,c_A}$ and $|\eta|_A$ values, the concentration effects of injected sample in PEV.

According to the approximate model of Krigbaum and Wall(11) on one hand and of Cragg and Bigelow (12) on the other, the reduced specific viscosity of a solution formed by polymer A (at c_A concentration) + polymer B (at c_B concentration) in a solvent is given by

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

where $t_{c_A+c_B}$, t_0, $|\eta|_A$, $|\eta|_B$, b_A, b_B, b_A' and b_B' are flow times through a capillary of a solution with c_A+c_B concentration and the pure solvent, intrinsic viscosities of polymer A and B, and viscometric interaction parameters of polymers A and B in the solvent respectively. w_i (i=A,B) is the weight fraction of polymer i in the polymeric mixture, that is $w_i = c_i(c_A+c_B)^{-1}$.

The last term in eq.(5) is added to account for the effects caused by higher concentration powers than lineal one on the reduced specific viscosity of polymer mixtures.

Recalling the definition of the reduced specific viscosity for polymer B (at c_B concentration) in a solvent

$$\frac{\eta_{sp}}{c_B} = \frac{(t_{c_B}/t_0) - 1}{c_B} = |\eta|_B + b_B c_B + b'_B c_B^2 + \cdots \tag{6}$$

the intrinsic viscosity of polymer A in a solution of polymer B (at c_B concentration) in a solvent should be given by

$$|\eta|_{A,c_B} = \lim_{c_A \to 0} \frac{t_{c_A+c_B} - t_{c_B}}{t_{c_B}\, c_A} = \frac{|\eta|_A + 2b_{AB}c_B + 3b'_{BBA}c_B^2 + \cdots}{1 + |\eta|_B c_B + b_B c_B^2 + b'_B c_B^3 + \cdots} \tag{7}$$

The above equation is similar to that reported by Dondos et al.(13) and Bohdanecky et al.(14) but with higher order concentration terms. b_{AB} and b'_{BBA} are assumed to be average values of the viscometric interaction parameters, namely, $b_{AB}=(b_A \times b_B)^{1/2}$ and $b'_{BBA}=(b'_B \times b'_B \times b'_A)^{1/3}$ (13,15). They, together with b_B and b'_B, characterize the interactions between like (BB) and unlike (AB, BBA) molecules respectively.

Since this paper is devoted to study the elution behaviour of a polymer A in a solution formed by itself at c_A concentration, we are only interested on the value of $|\eta|_{A,c_A}$, (see eq.(4)), which according to eq.(7) can be defined as:

$$|\eta|_{A,c_A} = \frac{|\eta|_A + 2b_A c_A + 3b'_A c_A^2 + \cdots}{1 + |\eta|_A c_A + b_A c_A^2 + b'_A c_A^3 + \cdots} \tag{8}$$

Recalling eq.(6) and the expression for reduced specific viscosity (eq.(1)), eq.(8) is transformed into:

$$|\eta|_{A,c_A} = \frac{|\eta|_A + 2k_A|\eta|_A^2 c_A + 3k'_A|\eta|_A^3 c_A^2}{1 + |\eta|_A c_A + k_A|\eta|_A^2 c_A^2 + k'_A|\eta|_A^3 c_A^3} \tag{9}$$

Finally, substitution of eq.(9) in eq.(4) gives:

$$V(c_A) = V(0) - \frac{1}{P} \log \frac{1 + 2k_A|\eta|_A c_A + 3k'_A|\eta|_A^2 c_A^2}{1 + |\eta|_A c_A + k_A|\eta|_A^2 c_A^2 + k'_A|\eta|_A^3 c_A^3} \tag{10}$$

Eq.(10) yields the $V(c_A)$ value as a function of $V(0)$, $|\eta|_A$, c_A, k_A and k'_A.

RESULTS AND DISCUSSION

Applicability of eq.(10) to predict concentration effects demands known values for both viscometric parameters, k_A and k'_A. As previously (3) discussed, the chances of finding appropriate k_A values for a given eluent-polymer sample-temperature system are remote, since besides the experimental incertitude accompanying k_A evaluation, k_A depends not only on polymer-solvent system but also on polymer molecular weight distribution, branching degree, velocity gradient,... (16,17). The above difficulties for finding appropriate k_A values extraordinarily increase regarding k'_A values, which are very scarce in literature or inexistent at all for most of the eluent-polymer systems with reported concentration effects. Because of the lack of reliable k_A and k'_A values, eq.(10) application seems useless for most of the systems or rests limited to some few particular eluent-polymer ones. In the following a semiempiric way is suggested intending to overcome that model limitation.

For non-rigid, non-interpenetrating spheres, the theory predicts (18) that $(k'_A/k_A^2) = 1$. Although few experiments have been devoted to ascertain such relationship, it seems that $(k'_A/k_A^2) \neq 1$ for polymer coils (19). In fact, an analysis by Sakai (20) suggests that $(k'_A/k_A^2) \leq 1/2$, where the equality is appropriate for a powers series expansion of Martin's equation, as pointed out by Norrby (21), with the result:

$$\frac{k'_A + A}{k_A^2} = 1 \qquad (11)$$

and A=0.125 for theta systems. From k_A and k'_A data on polystyrene and poly(methyl methacrylate) both in toluene and benzene, Maron and Reznik (22) confirm the validity of the above equation with A=0.09, as Baker also does, through a semiempirical model (23), with A=0.08 in a broad range of k_A and k'_A values (19).

In order to look for the most appropriate A value among the above scarce literature ones, experimental measurements on k_A and k'_A for poly(methyl methacrylate) narrow fractions, $I \leq 1.2$, in

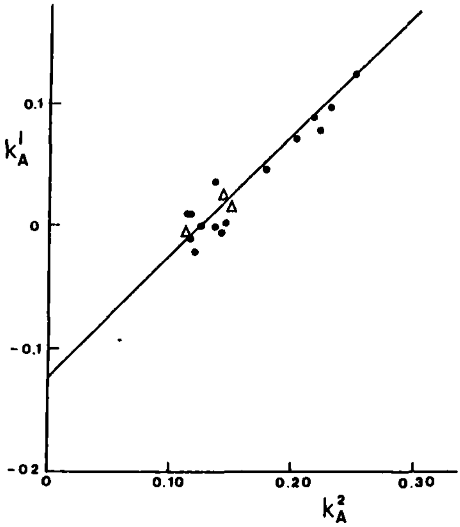

FIGURE 1. Empirical correlation between k_A and k'_A data for the PMMA in p-dioxane(●) and 1,2-dichloroethane(△) at 20 °C (PMMA molecular weight in the range 15000-150000).

p-dioxane and 1,2-dichloroethane at 20.0°C were undertaken. Obtained results again confirm eq.(11), as shown in fig.1, with a value A=0.122, in between the above literature ones. The substitution of k'_A, as given by eq.(11) with A=0.122, in eq.(10) easies its application since now it only depends on k_A. However, the difficulties, above pointed out, of finding reliable k_A data, prompted us to essay with k_A a parallel way to that followed for k'_A evaluation.

Huggins' constant is related to the viscometric expansion coefficient, α_η, through the equation of Imai (4):

$$k_A = k''\alpha_\eta^{-4} + C(1 - \alpha_\eta^{-2}) \qquad (12)$$

where k" and C are parameters independent on temperature, solvent power and polymer molecular weight. Theoretical evaluation for these parameters has not been yet done, though and through the analysis of experimental data for several polymer-good solvent systems, as polyisobutylene, polystyrene and poly(methyl methacrylate) in diverse good solvents, k" = 0.5 and C = 0.3 values have been obtained(24). In some cases, e.g., for poly(vinyl chloride), higher k" and C values have been reported (19).

On the other hand, α_η is defined by

$$\alpha_\eta^3 = \frac{|\eta|_A}{|\eta|_{A,\theta}} \tag{13}$$

where $|\eta|_A$ and $|\eta|_{A,\theta}$ are the intrinsic viscosities of polymer A in the studied solvent and in theta conditions, respectively. Likewise, $|\eta|_{A,\theta}$ may be evaluated from the unperturbated dimensions constant, K_θ, through

$$|\eta|_{A,\theta} = K_\theta M_A^{1/2} \tag{14}$$

where M_A is the polymer molecular weight.

Finally, k_A' substitution, as given by eq.(11) with A=0.122, in eq.(10) yields

$$V(c_A) = V(0) - \frac{1}{P} \log \frac{1 + 2b_A|\eta|_A c_A + (3k_A^2 - 0.366)|\eta|_A^2 c_A^2}{1 + |\eta|_A c_A + b_A|\eta|_A^2 c_A^2 + (k_A^2 - 0.122)|\eta|_A^3 c_A^3} \tag{15}$$

with

$$k_A = 0.5\left[\frac{|\eta|_A}{|\eta|_{A,\theta}}\right]^{-4/3} + 0.3\left[1 - \left(\frac{|\eta|_A}{|\eta|_{A,\theta}}\right)^{-2/3}\right] \tag{16}$$

recalling k_A, as given by eq.(12) with k" = 0.5 and C = 0.3, and α_η and $|\eta|_{A,\theta}$ definitions. $V(c_A)$ predicted for good solvent-polymer systems through the joint application of eqs.(15) and (16) no longer depends on k_A and k_A'. $|\eta|_{A,\theta}$ remains as the only parameter needed to evaluate concentration effects through this semiempiric model.

In order to discuss predicted concentration effects through this model, studied literature references have been grouped in three categories, as done before (3): i) Those in which both numerical values for $V(c_A)$ (usually in tables) and k_A values for the polymeric solutes are given. ii) Literature references in which $V(c_A)$'s are

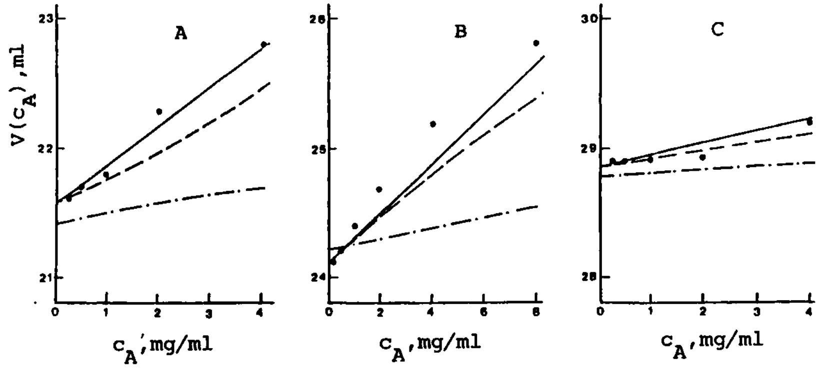

FIGURE 2. Experimental(1) (●) and predicted from references(1) (—·—·) and (3) (– – –) and through eqs.(15) and (16) (———) elution volumes for the systems: A) PS-867000; B) PS-498000; C) PS-200000 in THF.

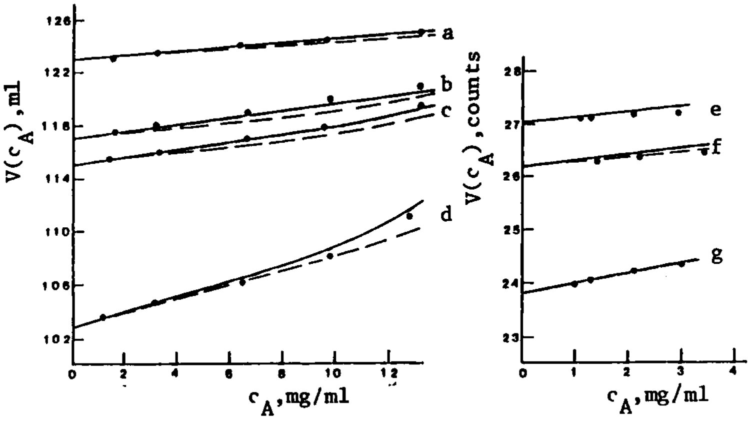

FIGURE 3. Experimental (●) and predicted from ref.(3) (– – –) and through eqs.(15) and (16) (———) elution volumes for the systems: a) PMMA-240000/THF; b) PMMA-440000/THF; c) PMMA-516000/THF; d) PMMA-246000/THF; e) PS-412000/THF; f) PS-620000/THF; g) PS-280000/THF. Experimental data for PMMA systems from ref.(26) and for PS ones from ref.(30).

TABLE 1

Parameters used for the Evaluation of Concentration Effects with eqs.(15) and (16)

System	Sample	P_1 ml^{-1}	$\|\eta\|$ ml/g	$K_\theta \times 10^3$ ml/g
PMMA/THF(26) Figure 3d	Fraction A-1 (M_w=2460000)	0.115	329(3)	59.2(25)
PS/TOL(27) Figure 4	PS-867000	0.108	218.7	74.5(25)
	PS-670000		181.7	
	PS-498000		146.7(27)	
	PS-392000		123.5	
	PS-318000		106.2	
	PS-200000		76.1	
PS/TOL(10) Figure 5c	PS-97200	0.068	42.8(10)	74.5(25)
PS/Benzene(28) Figure 7	PS-200000	0.400	80.7(28)	74.5(25)
	PS-270000		99.7	
PS/MEK(28) Figure 7	PS-160000	0.182	37.6	74.5(25)
	PS-200000		48.9(28)	
	PS-270000		52.3	
PS/Trichloro-benzene(8) Figure 8	PS-97200	0.081	38.0	74.5(25)
	PS-245000		74.0(8)	
	PS-780000		172.0	
Polybutadiene (PBD)/THF(29) Figure 8	PBD-17000	0.086	30.1(31)	166 (31)
	PBD-170000		192.6	

also given in tabulated form, but k_A for the measured polymers are not reported. iii) $V(c_A)$'s are given in figures.

The system polystyrene, PS, (M_w = 867000)/tetrahydrofuran, THF, falls into group i)(3). In figure 2A, concentration effects predicted through eqs.(15) and (16) are compared to experimental ones. A value K_θ = 74.5×10^{-3} ml/g (25) has been used for PS and the remaining data neccessary for eqs. (15) and (16) application are in table 3 in ref.(3).

In figures 2B, 2C, 3 and 4 elution volumes predicted by the present model are given for systems falling into group ii). Neccessary data for eqs.(15) and (16) application were in part, given in table 3 in ref.(3). A value $K_\theta = 59.2\times10^{-3}$ ml/g has been used for poly(methyl methacrylate), PMMA (25) and the remaining data are gathered in table 1.

Finally, in figures 5, 6, 7 and 8 predicted through eqs.(15) and (16) elution volumes are compared to experiment ones for systems falling into group iii). Neccessary data for eqs.(15) and (16) application are in table 1 and in table 3 in ref.(3).

As shown in the diverse figures, besides concentration effects predicted by the present model, those previously reported predicted by our previous simplified model and/or by other authors have been included, for comparison.

As expected, the differences between elution volumes predicted by the present model and by the previous simplified one are negligible up to $c_A \simeq 3\text{-}5$ mg/ml (depending on polymer molecular weight). Above these concentrations, elution volume curves predicted by eqs.(15) and (16) start to depart from those given by the simplified model, the former fitting closely to experimental ones up to $c_A \simeq 10$ mg/ml. This fact saves further discussion on the model goodness and only a last point deserves to be remarked. It is the easy application of the model since it only demands known values for K_θ and for the MHS equation, which are readily found in literature for most of the systems. Moreover, because of the good agreement between calculated through the present model and experimental concentration effects, a further application of concentration effects measurements in SEC may be profitable, as is the evaluation of k_A and k'_A parameters, which are scarce in literature and difficult to determine by experiments.

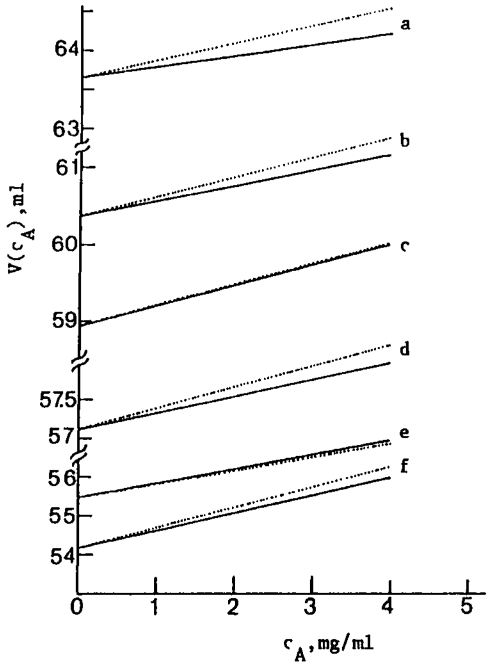

FIGURE 4. Experimental(27)(..........) and predicted through eqs.(15) and (16)(———) elution volumes for the systems: a) PS-200000; b) PS-318000; c) PS-392000; d) PS-498000; e) PS-670000 and f) PS-867000 in toluene(TOL).

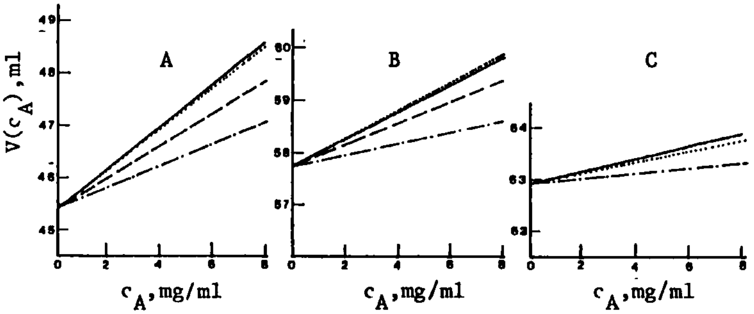

FIGURE 5. Experimental(10)(......) and predicted from refs.(10)(—·—·) and (3)(— — —) and through eqs.(15) and (16)(———) elution volumes for the systems: A) PS-498000; B) PS-320000 and C) PS-97200 in TOL.

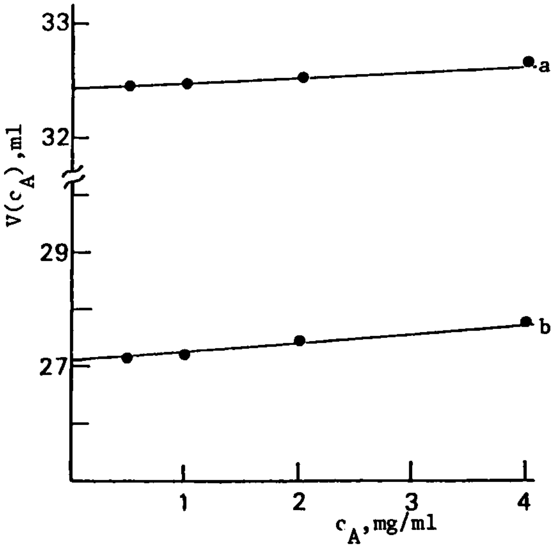

FIGURE 6. Experimental(2)(●) and predicted through eqs.(15) and (16)(———) elution volumes for the systems: a) PS-335000 and b) PS-498000 in butanone(MEK).

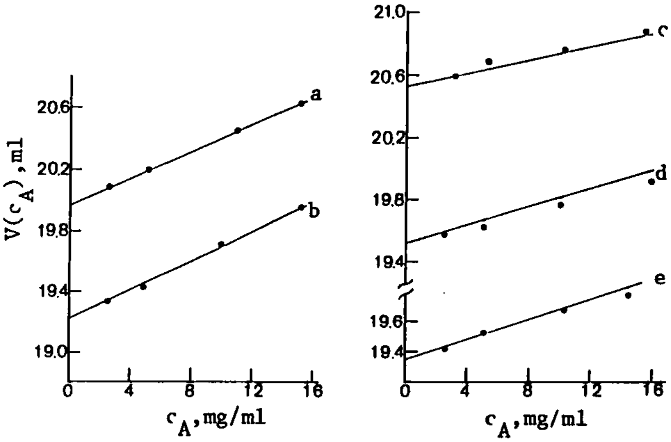

FIGURE 7. Experimental(28)(●) and predicted from eqs.(15) and (16) (———) elution volumes for the systems: a) PS-200000/benzene; b) PS-270000/benzene; c) PS-160000/MEK; d) PS-200000/MEK and e) PS270000/MEK.

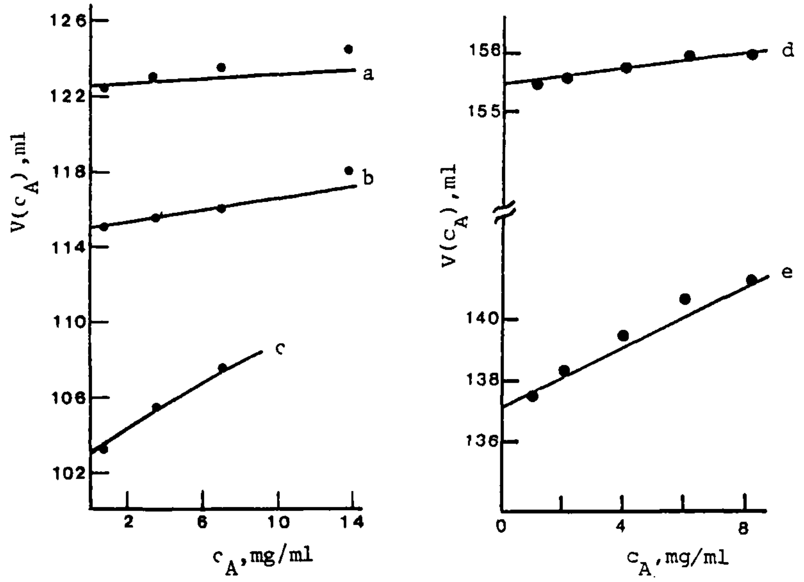

FIGURE 8. Experimental(●) and predicted through eqs.(15) and (16) (———) elution volumes for the systems: a) PS-97200/ trichlorobenzene(TCB); b) PS-245000/TCB; c) PS780000/TCB; d) PBD-17000/THF; e) PBD-170000/THF. Experimental data for PS systems from ref.(8) and for PBD ones from ref.(29).

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