A Qualitative Analysis of Secondary Mechanisms in SEC of Polymers Through the Mean Value of the Viscosimetric Exponent

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A Qualitative Analysis of Secondary Mechanisms in SEC of Polymers Through the Mean Value of the Viscosimetric Exponent*

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Size exclusion chromatography (SEC) universal calibration curves for poly(dimethyl-siloxane), polybutadiene and poly(2-vinylpyridine) samples have been obtained in columns packed with cross-linked polystyrene gel using cyclohexane, toluene, benzene, dioxane and tetrahydrofuran as eluents at 25°C. The eluents exhibit different thermo-dynamic quality for the polymeric solutes and for the gel matrix which is reflected in the values of their Mark-Houwink-Sakurada exponents a. The plots of log(hydrodynamic volume) *versus* retention volume for the polymeric solutes in different eluents are displaced to higher retention volumes than that of THF-polybutadiene (ideal SEC), evidencing the existence of secondary mechanisms. This elution behavior could be qualitatively explained through the mean average value $\bar{a}$, but a quantitative analysis requires the knowledge of solute–solvent, solvent–gel, solute–gel and ternary interaction parameters.

Keywords: SEC; Secondary mechanisms; Viscosimetric exponent; Interaction functions

INTRODUCTION

Size exclusion chromatography (SEC) is a widely used technique for determining the molecular weights of polymer molecules. SEC calibration is often achieved using the "universal calibration" method,[1] which assumes the hydrodynamic volume as the unique magnitude determining the size of the macromolecule, and therefore the retention volume. However, this approach fails when non-exclusion or secondary effects, such as partition and adsorption, interfere the pure size-exclusion process.[2-4] In the particular case that polymer solute–gel interactions are favored, the retention volumes will increase and the calibration curves will be shifted to the right of that in which only ideal SEC is the main mechanism.

However, it is well known that the hydrodynamic volume V_h is defined as the product of the molar mass of the macromolecule M and its intrinsic viscosity $[\eta]$ that is, $V_h = M[\eta]$. The intrinsic viscosity is experimentally obtained from specific viscosities and is related to the molar mass through the Mark-Houwink-Sakurada (MHS) equation, $[\eta] = KM^a$, K and a the MHS constants. The exponent a is a measure of the thermodynamic affinity or quality of the solvent for the polymer. Consequently, a is related with the solvent–polymer interaction. If an eluent is well compatible with the polymer sample ($a = 0.70 - 0.80$), and it is also good solvent for the gel matrix (basically crosslinked polystyrene) there is no preferential affinity of the mobile phase toward sample or stationary phase. Therefore, neither partition nor adsorption mechanisms will influence sample retention and separation will be exclusively controlled by solute size. A unique universal calibration curve will be achieved.

On the contrary, if the eluent is a poor solvent for the polymer, the solvent–polymer interactions are diminished and the polymer–gel interactions may play a more important role. In this case, secondary mechanisms other than pure SEC have to be taken into account.[2,3,5-13] The quantification of these mechanisms can be achieved by means of the distribution coefficient K_p, which has been mainly related to solute–gel interactions driven by enthalpic effects.[3,7,8] K_p has been explained in terms of solute–gel, eluent–gel and eluent–solute interactions by means of the interaction parameters independent of concentration χ_{23}, χ_{13} and χ_{12}, respectively. These

expressions have been proposed for partition mechanisms with soft highly-swollen gels.[14,15] Sometimes K_p has only been explained through the χ_{23} parameter[9] or through the interaction functions dependent on concentration, g_{23}, g_{13} and g_{12}.[16,17]

Recently, we have derived[18,19] an expression for K_p as a function of the binary and ternary interaction functions based on previously calculated interaction functions dependent on concentration.[19-23]

In this paper, we show for seven chromatographic systems eluent(1)-polymer solute(2)-gel packing (cross-linked polystyrene)(3) that, qualitatively at least, a mean average value of the MHS exponent may explain the SEC calibration curves but, quantitatively, it is also necessary to take into account all the thermodynamic interaction parameters.

EXPERIMENTAL

Chemicals

Polybutadienes (PBD) with polydispersity index between $1.03-1.05$ were purchased from Pressure Chemical (Pittsburgh, PA, USA) with weight-average molar mass, $M = 13400$, 67300 and 89960 and from Polymer Laboratories (Shropshire, UK) with $M = 18150$, 86500, 268000 and 1120000. Poly(dimethylsiloxanes) (PDMS) were supplied by Polymer Laboratories (Shropshire, UK) with $M = 7500$, 38400, 68500, 161000 and 480000 with polydispersity indexes 1.08, 1.08, 1.11, 1.17 and 1.42, respectively. Poly(2-vinylpyridine) (P2VPy) samples with $M = 7000$, 11000 and 33000 were purchased from Pressure Chemicals (PA, USA) and $M = 200000$ from Polysciences (PA, USA). Tetrahydrofuran (THF), benzene (Bz), toluene (TOL), 1-4 dioxane (Diox) and cyclohexane (CHX) from Scharlau (Barcelona, Spain) of chromatographic grade were used as sample solvents and eluents.

Chromatography

The liquid chromatograph consisted of a model 590 solvent-delivery system and a U6K universal injector, both purchased from Waters (Milford, MA, USA). Detection was carried out with a model

ERC-7522 Erma (Tokyo, Japan) refractive index detector which was set at an attenuation of 8x. The chromatograms were recorded by using a dual-channel recorder (Yokowaga Electric Works, Tokyo, Japan). The system was equipped with three μ-styragel columns 10^3, 10^4 and 10^5 Å nominal pore size (30 cm length $\times$ 0.78 cm i.d.) from Waters (Milford, MA, USA) which were packed with highly cross-linked styrene-divinylbenzene copolymer. All the solvents, used as mobile phases in the chromatographic experiments, were previously degassed and filtered by passing them under vacuum through a 0.45-μm regenerated cellulose filter from Micro Filtration Systems (Dublin, CA, USA). All chromatographic experiments were conducted at room temperature and the columns were equilibrated overnight prior to starting any experiment. Chromatograms were obtained at a flow rate of 1.0 mL min^{-1}, injecting 100 μL of polymer solution.

The dependence of elution volumes V_e on injected polymer concentration c, *i.e.*, concentration effects, could represent a further complicating factor in the quantitative evaluation of SEC polymer-gel interactions.[10] Moreover, the slopes of linear plots V_e *vs.* c depend on the thermodynamic quality of the eluent for the polymer.[24] In order to avoid concentration effects, all solute (polymeric) samples were injected at four different concentrations, and then extrapolated at zero concentration. For the set of the three μ-styragel columns used in this work, the void or interstitial volume V_0 and the pore volume V_p are 17.7 and 18.1 mL, respectively. The total exclusion limit (V_0) was evaluated by using polystyrene standard of a very high molar mass ($M = 2700000$), and the total permeation limit (V_T) by injecting small molecules as THF, TOL or Bz.

Viscosity Measurements

An automatic AVS 440 Ubbehlode-type capillary viscometer from Schott Geräte (Hofheim, Germany) at $25.0 \pm 0.1°$C was used to perform viscometric measurements. The stock solution was made by dissolving the polymer samples in the corresponding solvent up to a concentration of approximately 1.0 g dL^{-1}. At least six dilutions were obtained by adding the appropriate aliquots of solvent. Efflux time of the solvent was always above 100 s. To minimize drainage errors, of each solution, a 12 mL sample was loaded into the viscometer and

placed in the thermostated bath. Measurements started after an equilibration time of ca. 5 – 10 min and were continued until several flow time readings agreed to within 0.5%. The elution time of each solution is then determined as the average of several readings. The dilution and measurements are stopped when the viscosity difference of the sample solution and pure solvent drops below 10%.

RESULTS

The intrinsic viscosity for the different solvent – polymer pairs (see Experimental) have been evaluated by extrapolation to infinite dilution (zero solute concentration) of the Huggins plots: $\eta_{sp}/c = [\eta] + bc$, i.e., η_{sp}/c vs. c, being η_{sp} the specific viscosity, c the concentration of the solution and b a viscosimetric parameter. All the polymer samples gave good linear correlations ($r > 0.99$) when plotting $\log[\eta]$ vs. $\log M$. The K and a constants of Mark-Houwink-Sakurada (MHS) equation were evaluated for each polymer – solvent-temperature system, using the latter plot. Table I compiles the values of K and a at 25°C for the different binary systems studied. As pointed out, the constant a indicates the thermodynamic quality of the solvent by the polymer, or in other words, represents the magnitude of the solvent – polymer interactions. Therefore, the higher the a value the better the solubility of the polymer and the more favorable the interactions between both components of the system. As seen from the values in Table I, all solvents used except for cyclohexane exhibit higher thermodynamic affinity toward PS (the polymer of the packing) than toward other polymeric solutes (PBD, PDMS, P2VPy).

TABLE I   Mark-Houwink-Sakurada constants for the polymer systems studied at 25°C

System	$K\,(mL/g)^{(1)}$	$a^{(1)}$	System	$a^{(2)}$	System	$\bar{a}^{(3)}$
THF-PBD	0.0109	0.760	THF-PS	0.720	THF-PBD-PS	0.74
Bz-PBD	0.112	0.604	Bz-PS	0.740	Bz-PBD-PS	0.67
Diox-PBD	0.155	0.541	Diox-PS	0.690	Diox-PBD-PS	0.62
TOL-PDMS	0.0447	0.601	TOL-PS	0.740	TOL-PDMS-PS	0.67
Bz-PDMS	0.0579	0.572			Bz-PDMS-PS	0.66
CHX-PDMS	0.159	0.534	CHX-PS	0.479	CHX-PDMS-PS	0.51
Diox-P2VPy	0.1754	0.450			Diox-P2VPy-PS	0.57

[1] Experimental values. [2] From Ref. [26]. [3] Mean average value for the ternary solvent – polymer – polymer systems.

The analysis of the concentration effects on the elution volumes has been previously done for the same polymer–solvent systems (data not shown). This reveals that the polymer elution volume increases as the concentration increases and this effect is more pronounced with an increase of the polymer molar mass, as usually found in the literature.[24,25] Figures 1–2 depict the universal calibration curves made by plotting the hydrodynamic volume V_h (as $\log(M[\eta])$) *versus* elution volume extrapolated to zero polymer concentration for the seven studied systems. Data of molar masses have been given in the experimental part and the experimental intrinsic viscosities (in mL/g) are summarized by means of the MHS constants (Tab. I).

As can be seen from these plots, a different curve is obtained for each system instead of a unique calibration curve, which evidences the existence of nonideal size exclusion behavior or secondary mechanisms. In general, the elution volumes shift towards higher values than would be expected from ideal behavior, probably because of the appearance of gel–solute attractive interactions which causes a reversible adsorption of the solute onto the gel packing material.
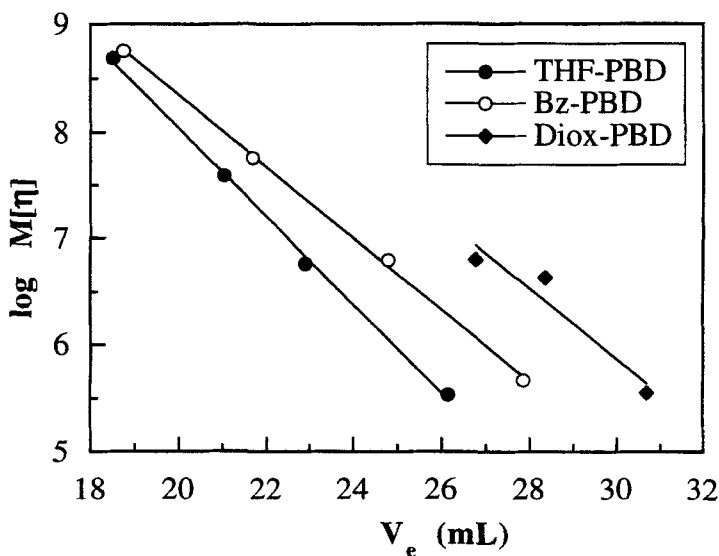

FIGURE 1   Universal calibration plots for PBD in three different solvents eluted in μ-Styragel columns (cross-linked PS gel).
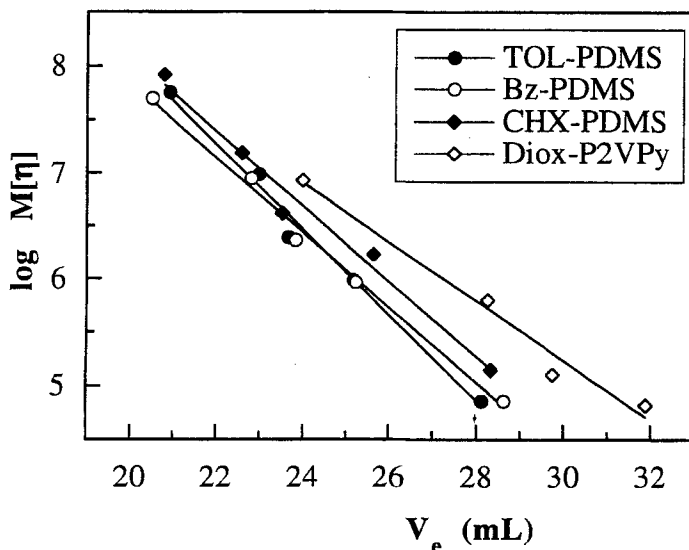
FIGURE 2 Universal calibration plots for PDMS and P2VPy in different solvents eluted in μ-Styragel columns (cross-linked PS gel).

The THF-PBD system shows the lowest V_e (highest a value in Tab. I), and has been taken as reference system in this work. Usually, the reference calibration curve is obtained with PS in a good solvent such as THF since it is supposed that this system exhibits neither favourable nor unfavourable interactions and the separation process is controlled exclusively by the size of macromolecules. We have found that the system PBD-THF shows an identical universal calibration curve as the PS-THF (in the same column). Therefore, the latter system has been assumed as reference system in order to avoid confusion.

DISCUSSION

Chromatographic separations of macromolecules by size relates to the selective distribution of macromolecules between the mobile binary phase (polymer solution outside the pore) and the stationary ternary phase formed by the mixture of polymer solution and gel packing.

This distribution process depends on the strength and type of interactions, and is described by

$$V_e = V_0 + K_D V_p \tag{1}$$

where V_0 is the interstitial or void volume, V_p is the packing pore volume, and K_D is the SEC distribution coefficient, equal to the ratio of the solute concentration in the stationary phase and in the mobile phase.

In SEC, separation is accomplished with respect to the hydrodynamic volume ($V_h = M[\eta]$) of the macromolecules. In the case of *ideal* SEC, separation is exclusively governed by conformational changes of the macromolecules and therefore, $K_D = K_{SEC}$. Since the conformational entropy decreases with decreasing polymer molar mass, the distribution coefficient of *ideal* SEC is $K_{SEC} < 1$. Accordingly, the SEC separation range is $0 < K_{SEC} < 1$, and the retention volume for ideal behavior is

$$V_e = V_0 + K_{SEC} V_p \tag{2}$$

If enthalpic effects, due to interactions between the polymeric solutes and the pore walls, take place, the distribution coefficient of *real* SEC is modified to $K_D = K_{SEC} K_p$, and the retention volume is as follows: [3]

$$V_e = V_0 + K_{SEC} K_p V_p \tag{3}$$

with $K_p < 1$ if solute–gel interactions are repulsive (*i.e.*, electrostatic type) or $K_p > 1$ when attractive (reversible adsorption of polymer onto the matrix packing, as can be seen in Figs. 1–2). Moreover, the distribution coefficients experimentally determined [3] are compiled in Table II for all the systems assayed. As seen from these values, the K_p values are, in general, greater than unity evidencing the adsorption mechanism besides the SEC behavior, and near to 1 for THF-PBD-PS which can be considered as ideal SEC mechanism and taken as reference system.

From a thermodynamic point of view and in the framework of the Flory-Huggins theory, we have recently derived [18, 19] an expression for the partition coefficient K_p when secondary mechanisms appear

TABLE II Experimental elution volumes V_e and distribution coefficients* K_p at three hydrodynamic volumes V_h for the different systems assayed

System	$V_h = 10^6$		$V_h = 10^7$		$V_h = 10^8$	
	V_e (mL)	K_p	V_e (mL)	K_p	V_e (mL)	K_p
THF-PBD	24.96	1.006	22.53	0.992	20.10	0.958
Bz-PBD	27.03	1.293	24.02	1.298	21.02	1.325
Diox-PBD	29.50	1.636	26.72	1.853	23.94	2.490
TOL-PDMS	25.35	1.061	23.00	1.089	20.66	1.181
Bz-PDMS	25.47	1.077	22.78	1.043	20.11	0.962
CHX-PDMS	26.06	1.159	23.40	1.171	20.75	1.217
Diox-P2VPy	27.24	1.318	23.64	1.215	20.04	0.923

*K_p determined from Eq. (3) with K_{SEC} values from the reference system THF-PBD at the three V_h. $K_{\text{SEC}} = 0.40$, 0.27 and 0.14, respectively.

for a ternary system formed by solvent(1) – polymer(2) – gel(3)

$$\ln K_p = \frac{V_2}{V_1} \phi_3 \{ -1 + g_{12} + g_{13} - g_{23} - g_T \} \tag{4}$$

where ϕ_3 is the fraction of the gel matrix solvated by the eluent taking part in the separation process, V_2/V_1 is the ratio of the molar volumes of components 1 and 2, g_{ij} $(i,j = 1, 2, 3)$ are the interaction functions between the species i and j from the Flory-Huggins approach, and g_T is the ternary interaction function, the physical meaning of which is still unclear but includes interactions that are ternary in nature. [27–30]

Thermodynamically, the requirement for obtaining a multicomponent solution is that the Gibbs free energy of mixing ΔG must be negative. Therefore, let us, briefly, describe this magnitude for the mixing of a polymeric solute(2) and of a polymeric network(3) in two different solvents named A and B, in order to discuss how binary interactions could influence each other. For component 2, ΔG is given by

$$\Delta G = \text{RT} \left\{ \phi_i \ln \phi_i + \frac{V_i}{V_2} \ln \phi_2 + \phi_i \phi_2 g_{i2} \right\} \tag{5a}$$

and for component 3

$$\Delta G = \text{RT} \left\{ \phi_i \ln \phi_i + \frac{V_i}{V_3} \ln \phi_3 + \phi_i \phi_3 g_{i3} \right\} \tag{5b}$$

and $i = (A, B)$ denoting two different solvents.

If we assume that solvent A better solvates both the polymer and the gel than does solvent B, the corresponding ΔG (Eqs. (5a) or (5b)) will be more negative, that is, the solvent-polymer interaction functions g_{A2} and g_{A3} will be lower than g_{B2} and g_{B3}. Therefore, in the light of Eq. (4), the values of K_p will be higher for the same polymer and gel in solvent B than in solvent A. This behavior is in agreement with the experimental results given in Figures 1–2 and in Table II. For example, by comparison of systems THF-PBD with Diox-PBD, we can see that THF (solvent A) is a better solvent for both PBD and PS (see the a values in Tab. I) than Diox (solvent B), in which the universal calibration curve is shifted toward higher values of V_e. Consequently, K_p value is higher at any V_h in the latter system.

Moreover, the results are in agreement with the well-known statement[2–4] that for a given polymer and gel, K_p increases when the thermodynamic quality of eluent toward polymer sample decreases (see Tabs. I and II and $\bar{a}$ and K_p values). Furthermore, we also think that if polymer and gel are both poorly solvated by solvent B than by solvent A (or $g_{B2} > g_{A2}$ and $g_{B3} > g_{A3}$), it is also possible to predict higher (or more favorable) polymer–gel interactions in the former solvent. In consequence, $g_{23(B)} < g_{23(A)}$ and also $g_{T(B)} < g_{T(A)}$ (since g_{23} is included in g_T) which also implies a concomitant increase in the K_p values for solvent B, in the light of Eq. (4).

From a thermodynamic viewpoint, when eluent becomes poorer for polymer and/or for gel packing, the interaction parameters g_{12} and g_{13} increase whereas g_{23} and g_T decrease, leading both to a rise of the distribution coefficient values, K_p. This was many times experimentally observed. For the ternary systems here studied, both g_{23} and g_T functions have been evaluated[18] by analyzing the composition of two equilibrium phases by liquid chromatography.[20–23] Nevertheless, in some systems the quantitative influence of g_{23} on K_p cannot be accurately predicted since the g_{23} value is also influenced by g_T, and, usually, both parameters cancel each other[22] due to their similar absolute values but of opposite sign. Therefore, in these cases, the prediction of K_p can be exclusively made through the values of the solvent–polymer interaction functions, g_{12} and g_{13}, *i.e.*, it could be based on the thermodynamic quality of the solvent by the polymer, at least qualitatively.

According to the above considerations, next we intend to explain the polymer elution behavior in SEC through the MHS exponent which represents the thermodynamic affinity of the solvent by the polymeric solute. The size parameter in SEC is given by the hydrodynamic volume V_h which is related to the MHS constants through

$$V_h = M[\eta] = KM^{(1+a)} \qquad (6)$$

According to Eq. (6), for a given molar mass, the higher the a value the higher the V_h indicating larger expansion of the macromolecular coil and its stronger interaction with the solvent/eluent. Table I shows experimental values of a for the systems solvent(1)–polymer(2) measured in this work, and from the literature[26] for eluent(1)–PS gel(2). In addition, we consider the arithmetic average value $\bar{a}$ for a system solvent(1)–polymer(2)–PS(gel matrix)(3) calculated from a values for the corresponding binary systems (Tab. I). As $\bar{a}$ decreases the solvent becomes poorer both for the polymer and for the gel matrix, favoring the solute–gel interactions and shifting the elution volumes to higher values. This behavior has been experimentally evidenced in Figures 1 and 2, where the elution volumes of different systems follow decreasing $\bar{a}$ values for a given V_h. The only exception is the Diox-P2VPy-PS system. To explain this apparent anomaly, let us analyze the values of the term $-g_{23} - g_T$ for the systems Diox-PBD-PS and Diox-P2VPy-PS. The former system has $-g_{23} - g_T \approx -0.24$ and the latter one is -0.90. Hence, keeping in mind Eq. (4) and assuming that the ratio $(V_2/V_1)\phi_3$ is similar for a given V_h,[18] these values would explain that the experimental V_e (or K_p) will increase in Diox-PBD-PS with respect to Diox-P2VPy-PS. Other authors,[10] are currently investigating the anomalous behavior between rather nonpolar polystyrene and the highly polar poly(2-vinyl pyridine) polymers in order to better understand the interactive properties of the SEC gels.

However, when comparing the systems CHX-PDMS-PS ($\bar{a} = 0.51$) and Bz-PDMS-PS ($\bar{a} = 0.70$), the calibration curve for the former system is shifted to higher V_e values, in agreement with the expectation. Still the differences between courses of these universal calibration curves are smaller than that expected from the numerical

difference in their $\bar{a}$ values. Again, we have to discuss this fact on the basis of the $-g_{23} - g_T$ values being equal to -0.20 for CHX-PDMS-PS and 3.08 for Bz-PDMS-PS[18] which is significantly more important and decreases K_p (or V_e) from Eq. (4) against expectation based on the $\bar{a}$ values. In the three remaining systems, the values of $-g_{23} - g_T$ have been also determined[18] but they have not been here included since both cancel each other and do not influence the K_p values.

It can be concluded that, at least qualitatively, the MHS exponent or its mean value $\bar{a}$, representing the thermodynamic quality of the eluent toward both solute the gel can explain the chromatographic results with a rather good approximation. However, in order to realize a quantitative analysis of the experimental K_p data, it is necessary to take into account the values of the thermodynamic parameters (g_{ij} and g_T) accounting for all the possible interactions between the components of the chromatographic systems. This work is currently in progress.

Acknowledgments

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