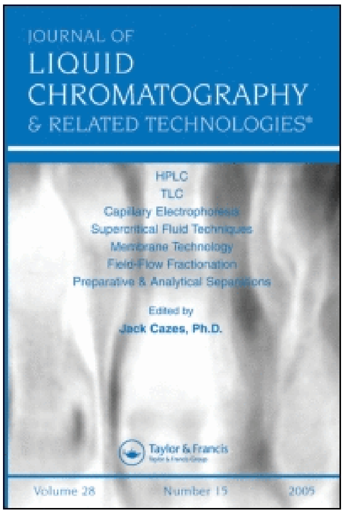

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

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To cite this Article Chiantore, Oscar(1984) 'Polymer-Substrate Interactions in Size Exclusion Chromatography with Silica Gels and Pure Solvents', Journal of Liquid Chromatography & Related Technologies, 7: 1, 1 — 11
To link to this Article: DOI: 10.1080/01483918408073946
URL: http://dx.doi.org/10.1080/01483918408073946

JOURNAL OF LIQUID CHROMATOGRAPHY, 7(1), 1-11 (1984)

POLYMER-SUBSTRATE INTERACTIONS IN SIZE EXCLUSION CHROMATOGRAPHY WITH SILICA GELS AND PURE SOLVENTS

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ABSTRACT

The retention volumes of polystyrene, poly(α-methylstyrene) and poly(methylmethacrylate) molecules eluted with different pure solvents on silica size exclusion chromatography columns have been measured. Departures from the universal calibration plot due to polymer adsorption onto the silica substrate are found in some solvent systems, when the polymer gel interactions overcome the solvent gel ones. The competition between the interactions developed in the systems is adequately expressed through the solubility parameters of the polymers and of the solvents.

INTRODUCTION

In size exclusion chromatography secondary effects must be carefully avoided especially when the polymer molar mass distributions are calculated with the universal calibration curve, log (hydrodynamic size) vs. elution volume, based on the elution of polystyrene (PS) standards. If steric exclusion is not the only process controlling the polymer retention in the column, it is known that the elution volumes of the samples will not fit the universal calibration plot. The main processes which can superimpose to the

0148-3919/84/0701-0001$3.50/0

size fractionation are the partition ones, where the solute molecules show a different solubility in the liquid stagnant phase, and the adsorption of solute molecules interacting with the gel structure.

When working with inert packings, such as the crosslinked polystyrene gels, it has been reported(1) that both partition and adsorption can be responsible for shifts towards higher elution volumes for the polymer samples and often it is difficult to distinguish between the two effects.

With active packings, like silica gels, displacements to both higher and lower elution volumes in respect of a reference system following the steric exclusion separation, have been reported(2). The changes in the elution volumes of polystyrene, polydimethylsiloxane and polymethylmethacrylate samples eluted in several pure and mixed eluents on silica-based chromatographic columns have been thoroughly investigated by Figuerelo and coworkers(3,4), who took into account the interactions developed between the gel, the polymer and the eluent. The solvent-gel interactions were expressed through the eluent strength ε° (5), the polymer-solvent interactions through the exponent α of the viscometric equation for the given system, and the solute-gel interactions through the polymer solubility parameter, δ. The experimentally found lower elution volumes, in respect of the chosen reference system, occur in mixed solvent media with high ε° and low α values, and could be attributed to partitioning of the solute molecules preferring the mobile phase to the liquid stagnant phase. With solvents having low ε° values, higher retention volumes were found and partition plus adsorption effects were considered to be responsible for them. When the adsorption processes become predominant, the influence of hydrogen bonding was also stressed(6).

By looking at the interactions which can take place in the elution with pure solvents of neutral polymer molecules on active gels, it can be considered that any deviation occurring in respect of a purely steric exclusion mechanism results in higher retention volumes of the samples. As solvent composition changes cannot occur, partition will not play any role in the process; on the other hand the surface activity of the gel toward solute molecules can change according to the eluent and will then compete with the polymer-solvent interactions in the system. Retardation of the polymer elution volumes will be then the result of polymer gel interactions prevailing over the polymer-solvent ones.

In this paper results on the elution behaviour of PS, poly(α-methylstyrene), (Pα MS), and poly(methylmethacrylate), (PMMA), samples in different pure solvents with microparticulate silica packings are reported, and the interactions developed in the different systems are discussed on the basis of the agreement, or disagreement, of the polymer retention volumes with the universal calibration plot of PS in tetrahydrofuran.

EXPERIMENTAL

Narrow distribution polymer standards were employed throughout this investigation. The PS standards were obtained from Arro Laboratories (Joliet, Illinois); PαMS and PMMA samples were supplied from Polymer Laboratories (Shrewsbury, England).

Spherical silica gels having average particle diameter of about 10 μm (Lichrospher, E. Merck, Darmstadt, Germany) were slurry packed on stainless steel columns. Four individual columns (25 cm length, 0.46 cm I.D.) were used, with different pore size silicas. The mean pore size of the gels employed were 10 nm, 50 nm and 100 nm.

The measurement of the elution volumes of the polymers were run on two different column combinations: the first one consisted of 4 columns in series (2 x 100 nm, 1 x 50 nm, 1 x 10 nm); the second one was a two column system (100 nm, 50 nm).

All the solvents were analytical grade reagents (C. Erba, Milan, Italy) and were used as received, with the exception of tetrahydrofuran which was stored with KOH and distilled under CaH_2.

The chromatographic elutions were performed with a Waters M45 pump, a Rheodyne injection valve and a Siemens differential refractometer detector, at a flow rate of about 0.5 cm^3 min^{-1}. Injection volumes of 50 $\mu\ell$ on the 4 column system, and of 20 $\mu\ell$ on the two column set were used, with polymer concentrations of 0.1% w/v.

The elution volumes of the samples were determined during each run by measuring the time for collecting a given amount of effluent. All the measurements were done in triplicate, and the reproducibility of the elution volumes was better than 1%.

RESULTS AND DISCUSSION

The elution behaviour of the PS and PαMS molecules in toluene was compared with that of PS in tetrahydrofuran. Both tetrahydrofuran and toluene are good solvents for PS, as indicated by the values of the exponent of the viscometric equations which are, at 25°C, $\alpha = 0.723$ in tetrahydrofuran(7) and $\alpha = 0.73$ in toluene(8). Toluene is also a good solvent for PαMS ($\alpha = 0.744$(8)), therefore favourable polymer-solvents interactions are expected in all these systems. On the other hand, the eluent strength of tetrahydrofuran, $\varepsilon^{\circ} = 0.57$(5), is higher than that of toluene, $\varepsilon^{\circ} = 0.29$(5) meaning that the latter solvent has a lower affinity for the silica substrate. The results of the polymer elutions are reported in Fig. 1, in terms of log ($[\eta]$ M) vs. elution volumes, V_e. The solid line represents the curve for PS in tetrahydrofuran, and the points are for the elutions in toluene. It can be seen that the elution volumes of PS in toluene are generally displaced to higher values in respect of those of PS in tetrahydrofuran, the differences being small but, owing to the limited volumes involved in SEC with micropackings, significant. If the average molar masses of PS samples eluted in toluene ought to be calculated by means of the universal curve based on PS/tetrahydrofuran, significant errors would result.

The P$^{\alpha}$MS samples eluted in toluene seem to agree better with the PS/tetrahydrofuran system in the lower part of the plot (molar masses $< 10^5$), whereas the high molar mass (7.6×10^5) sample shows a behaviour more similar to that of the system PS/toluene.

From the results of Fig. 1 it appears that, notwithstanding the favourable polymer-solvent interaction, PS molecules in toluene are interacting with the gel more than in tetrahydrofuran; according to the differences in the ε° values of the solvents, tetrahydrofuran will successfully compete with the PS molecules in the interactions with the silica.

The competition between the different binary interactions taking place in every solvent-polymer-gel system can be better expressed by considering the values of the solubility parameter, δ, of the solvents and of

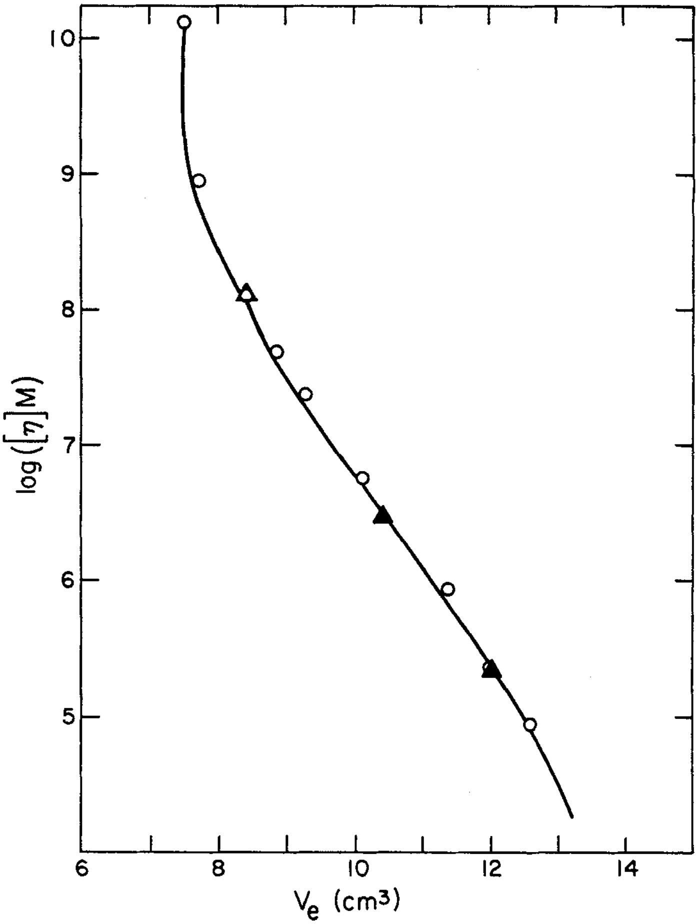

Figure 1 Elution behaviour of PS (o) and PαMS (▲) in toluene in conparison with PS in tetrahydrofuran (solid line). Column system: 2 x 100 nm, 50 nm, 10 nm.

the polymers(9). In this way one can describe polymer-solvent, polymer-gel and solvent-gel interactions by using the same parameter, therefore allowing more direct comparisons.

For the systems of Fig. 1, the values of δ which are of interest are reported in Table 1. The δ for PαMS was not found in the literature, but its value should be close to that attributed to the monomer, α-methylstyrene.

TABLE 1

Values of the Solubility Parameters for the Polymers and Solvents Employed (from Ref. 8 and 10)

	δ	δ_d	δ_p	δ_h
		$(J \cdot cm^{-3})^{1/2}$		
Polystyrene	18.6	17.6	6.1	4.1
Poly(methylmethacrylate)	19.4	18.8	10.2	8.6
α-methylstyrene	17.4			
Toluene	18.2	17.3-18.1	1.4	2.0
Tetrahydrofuran	19.5	16.8-18.9	5.7	8.0
2-Ethoxyethanol	24.3	16.1	9.2	14.3
Acetonitrile	24.3	15.4-16.2	18.0	6.1

The affinity between PS, PαMS and the solvents is indicated by the similarity of the δ values, but as to the interactions with the gel, the strongest ones are those of tetrahydrodrofuran which has the highest δ value in the systems hereby considered. This is of course the result of the polarity of tetrahydrofuran, and the effect is particularly evident by looking at the values of the contributions to δ due to the polar forces and to hydrogen bonding, δ_p and δ_h respectively, which are also shown in Table 1 together with the contribution δ_d of the dispersion forces. The comparison of the solubility parameter values shows that in tetrahydrofuran the PS molecules will not preferentially interact with the silica stationary phase, therefore the retention volumes are only size-exclusion dependent. In toluene solutions, on the other hand, the interactions between PS and silica gel, as expressed especially by the δ_p and δ_h values, are slightly prevailing over the solvent-gel ones, thus explaining the retardation of the polymer molecules in respect of the elutions in tetrahydrofuran. The values of the different contributions to the solubility parameter of α-methylstyrene are not known, and therefore the discussion for PαMS cannot go too far, but the comparison of the δ values in Table 1 seems to indicate that PαMS molecules in toluene shouldn't interact with the gel, and agreement with the elution curve of PS in tetrahydrofuran is expected.

In the case of polar solute molecules eluted on silica gel columns the retention volumes even in tetrahydrofuran can be affected by secondary non-exclusion effects. In Fig. 2 the behaviour of PMMA narrow distribution molecules in tetrahydrofuran is shown, compared with the system PS/tetrahydrofuran as a reference. The α value for PMMA/tetrahydrofuran at 25°C is 0.72(11), practically identical to that of PS/tetrahydrofuran, and the solubility parameter δ of PMMA is fully comparable with that of tetrahydrofuran (see Table 1), but the PMMA molecules are more retained than the PS ones. The explanation can be found by looking at the values of the contributions δ_p and δ_h for the polymers and for tetrahydrofuran: whereas the δ_h term for PS is negligible compared to that of the solvent, tetrahydrofuran, the d_h term for PMMA slightly overcomes that of tetrahydrofuran, and also δ_p is consistently higher for PMMA. The stronger polar interactions and hydrogen bonding capability of PMMA in respect of tetrahydrofuran can be therefore responsible of the polymer elution retardation in respect of the PS/tetrahydrofuran system. Retarded elutions of PMMA in several eluents, in respect of PS, were already discussed by Figuerelo et al.(4) but no data were reported on the elution of PMMA in tetrahydrofuran. The latter is the most common solvent employed in polymer SEC, and the results here reported show that with non deactivated silica packings molar mass distributions of PMMA in tetrahydrofuran cannot be correctly calculated by using the PS-based universal calibration plot.

The competition in developing specific polar interactions between the gel active sites and the eluent or the polymer molecules and the importance of these interactions in respect of the polymer-solvent ones can be further tested by considering the elution behaviour of a polar polymer in some polar

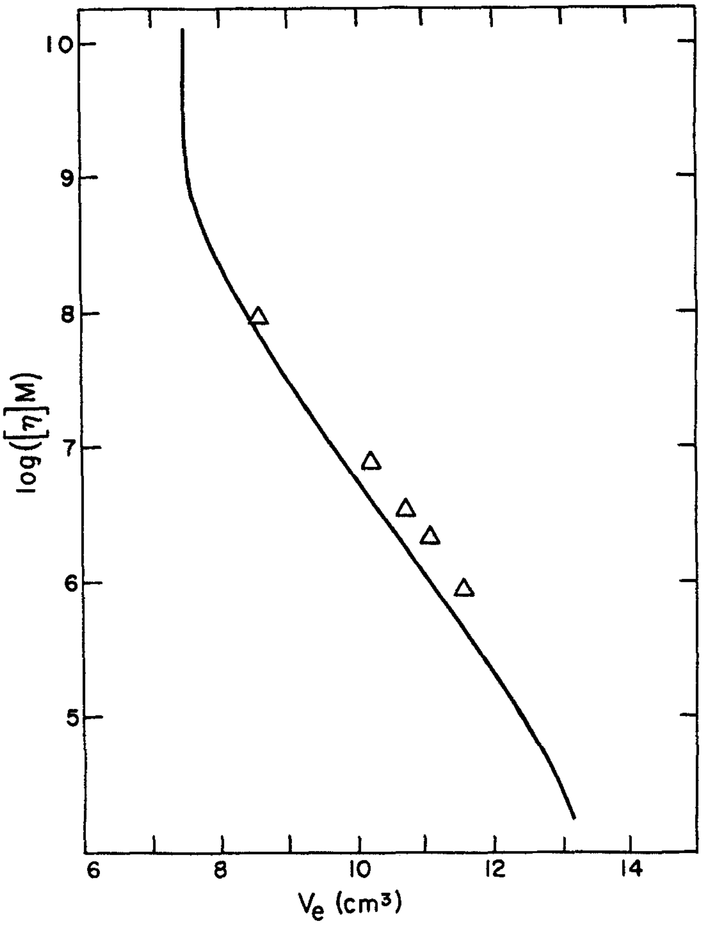

Figure 2 Elution behaviour of PMMA in tetrahydrofuran (Δ). Solid line represents PS in tetrahydrofuran. Column system: 2 x 100 nm, 50 nm, 10 nm.

eluent which at the same time is poor solvent for the polymer. For PMMA polymers two solvents have been found suitable for this comparison: acetonitrile and 2-ethoxyethanol. Both these eluents are practically theta solvents for PMMA at room temperature(12,13), (α = 0.5), and they have higher eluent strengths than tetrahydrofuran: ε° = 0.65 for acetonitrile, whereas for 2-ethoxyethanol ε° should be not very different from the value ε°

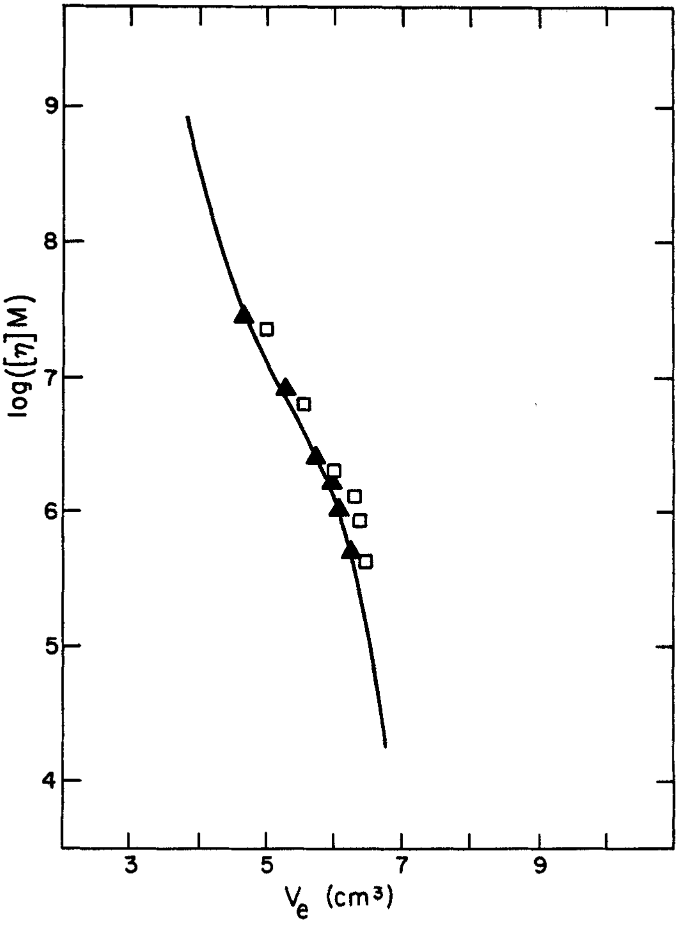

Figure 3 Elution of PMMA in 2-ethoxyethanol (▲) and in acetonitrile (□) compared with the PS/tetrahydrofuran line. Column system: 100 nm, 50 nm.

= 0.74(14) of the omologue compound 2-buthoxyethanol. Polymer-solvent interactions are then low, and solvent-gel interactions should be strong, as is also shown by the δ values in Table 1, which are higher than that of PMMA. But looking at the values of the hydrogen-bonding term δ_h for the two solvents in the same Table 1, it appears that 2-ethoxyethanol, being both proton acceptor and donor, has a definite higher affinity for the gel than acetonitrile; the δ_h value of the latter solvent is also lower than that of PMMA. The retention volumes of PMMA in acetonitrile are then expected to be higher than those in 2-ethoxyethanol , and this is indeed experimentally found in the results reported in Fig. 3. Notwithstanding the high overall polarity of acetonitrile, adsorption of PMMA on the silica occurs in this solvent, whereas the opposite happens in 2-ethyoxyethanol solutions where the polymers elute regularly and the points fit the PS universal curve.

CONCLUSIONS

The retention volumes of polymer molecules eluted on silica gel columns with pure solvents can be adequately explained through the competition of interactions with the gel between the eluent and the solute, as expressed by the solubility parameters of solvents and polymers, and particularly by the contributions to δ due to polar and hydrogen-bonding interactions. Adsorption on the silica surface becomes particularly relevant with polar polymers, and therefore in these cases SEC should be performed with solvents having higher possibility than the polymers of forming hydrogen-bonds in order to completely suppress the polymer-gel interactions.

The adsorption of PMMA onto silica substrates from tetrahydrofuran, between other solvents, has been also recently measured with static experiments(15); acid-base interactions between solvent, polymer and filler surface were proposed as a way of explaining all polar and hydrogen-bonding interactions. Yet the evaluation of the interactions through the solubility parameters as proposed here seems to be simpler and of more practical value for the chromatographic interpretation.

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