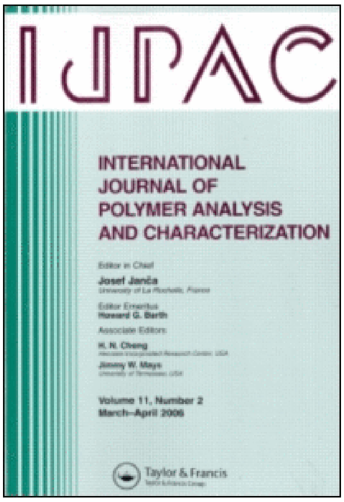

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Katia Baran[ab]; Serge Laugier[a]; Henri Cramail[b]
[a] Laboratoire de Modélisation Avancée des Systèmes Thermiques et Ecoulements Réels, Talence cedex, France [b] Laboratoire de Chimie des Polymères Organiques, UMR 5629, ENSCPB, Université Bordeaux-1, Talence cedex, France

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Liquid Chromatography of Polymers at the Exclusion – Adsorption Transition Point: Physicochemical Interpretation*

KATIA BARAN [a,b], SERGE LAUGIER [a] and HENRI CRAMAIL [b,†]

*[a]Laboratoire de Modélisation Avancée des Systèmes Thermiques
et Ecoulements Réels;
[b]Laboratoire de Chimie des Polymères Organiques, UMR 5629,
ENSCPB, Université Bordeaux-1, Avenue Pey Berland, BP 108,
F-33402 Talence cedex, France*

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This paper deals with liquid chromatography of polymers at the exclusion–adsorption transition point (LC EATP). In order to better understand and define this specific elution mode, all polymer chains with the same chemical structure are eluted at the identical retention time whatever their molar mass, a physicochemical study dealing with solution properties of polymers was undertaken. A correlation between polystyrene dimensions and this chromatographic mode was attempted by viscometry and light scattering measurements. The influence of temperature was also studied. It was demonstrated that EATP is obtained for specific values of polymer/adsorbent interactions, for a given eluent desorli/adsorli, and for a "critical polarity" of the eluent.

Keywords: Liquid chromatography; Critical conditions; Polymer/absorbent interactions

INTRODUCTION

Liquid chromatography of polymers at the exclusion–adsorption transition point (LC EATP) is now a well-established technique to differentiate macromolecules according to their chemical

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[†] Corresponding author.

composition,[1–4] functionality[5–8] or any "heterogeneity", without taking into account the molar distribution of the whole sample. This technique can be used to determine the molar mass distribution of the polymer chains, bearing the same heterogeneity. Therefore, this possibility to discriminate each kind of macromolecules has given rise to strong interest in the polymer community.

It is worth noting that this technique was first shown by Belenky *et al.* [9] by thin layer chromatography. The key of this fractionation is the use of a chromatographic eluent with a very specific composition. In most cases, the eluent is a binary mixture of solvents:[10] an adsorli and a desorli. The former exhibits low affinity towards the stationary phase and therefore eases the polymer adsorption. The latter possesses high affinity to the column packing and, consequently, enables the desorption of the polymer chain. At the eluent composition corresponding to the EATP, macromolecules of identical chemical structure are eluted with the same retention time whatever their molar mass (Fig. 1). Consequently, polymer chains exhibiting different functionality or chemical compositions could be easily differentiated.

More recently, the use of coupling techniques to discriminate macromolecules has emerged. Indeed, it is of particular interest to fractionate, first, the polymer chains according to their compositional

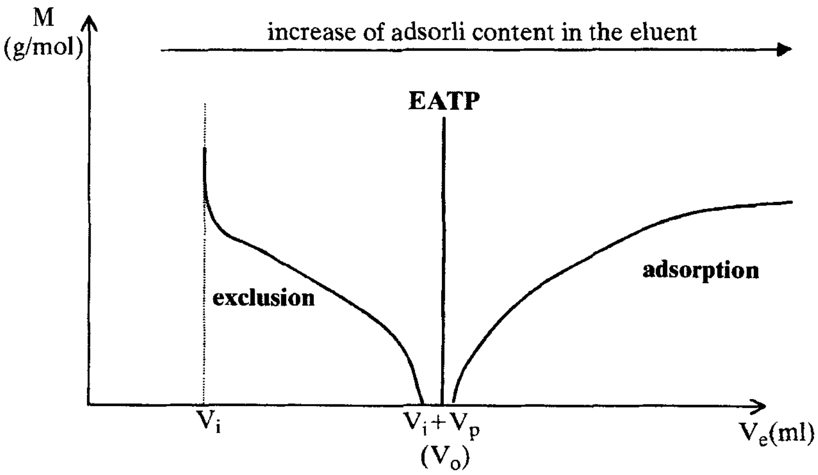


FIGURE 1 Calibration curves $M=f(V_e)$ of polymer chains in three elution modes in liquid chromatography: exclusion, EATP and adsorption.

heterogeneity – LC EATP technique – and, secondly, to determine the molar mass distribution of the polymer chains having the same heterogeneity – SEC technique.

The LC EATP phenomenon has also attracted attention from theoreticians [11–13] who developed different models to explain this peculiar elution mode. Since the behavior of the polymer chains, under these specific conditions, was not completely clear, we decided to elucidate some questions. To that end, a viscometric and light scattering analysis of model polystyrene standards in eluents of "critical" compositions corresponding to the EATP phenomenon, were carried out. The determination of the polymer molecular dimensions and their correlation with the chromatographic behavior is studied in this paper.

EXPERIMENTAL

Solvents

Toluene 99.8% (Scharlau, Spain), methyl ethyl ketone (MEK) 99% (Lancaster, France), ethyl acetate (EtAc) 99.5% (Scharlau, Spain), CH_2Cl_2 stabilized with 50 ppm of amylene (Scharlau, Spain), and *n*-hexane 96% (Scharlau, Spain) were used as received. Tetrahydrofuran (THF) stabilized with 0.025% of butylated hydroxytoluene (Baker Analyzed Reagent) was distilled over calcium hydride before use. Solvent mixtures were prepared by weighing.

Polymer Samples

Polystyrenes (PS) (PolymerExpert, France; Cluzeau, France) ranging from 3700 to 3.22×10^6 g/mol and of narrow molar mass distribution ($M_w/M_n < 1.1$), were dissolved in the eluent mixtures at a concentration of 0.15–0.3 wt% just before analysis.

HPLC Equipment

LC EATP experiments were performed on a high pressure liquid chromatography (HPLC) system constituted of either a Varian (USA) model 9002 pump or a JASCO (Japan) model PU-980 pump and a

Rheodyne six-port injection valve with a 20 μL sample loop. A Shimadzu (Japan) SPD-6A and a JASCO UV-975 ultra-violet spectrophotometric detectors, set at 261 nm were used for the detection. A Varian (USA) RI-4 refractometer was used for the polystyrene detection in the case of toluene as a solvent. The flow rate was 1 mL/min. Two Nucleosil (Macherey-Nagel Germany) columns (silica and silica aminopropyl), dimensions 250 × 4.6 mm, filled with particles of 5 μm size and of 100 Å porosity were used for the experiments. The columns were thermostated with a CROCO-CIL oven (Cluzeau, France).

Light Scattering

Dimensions of the polystyrene samples were measured by the scattering of light in various solvent mixtures and particularly in those corresponding to LC EATP conditions. The light scattering apparatus is composed of a Varian model 9002 pump fitted with a 1.5 mL sample injection loop and a multi-angle LLS Wyatt(USA) model DawnDSP detector, fitted with a laser photometer ($\lambda_o = 632.8$ nm). A Nucleosil Silica-C_{18} (Macherey-Nagel, Germany) guard column, dimensions 11 × 4 mm, filled with particle of 5 μm size and of 100 Å porosity was used for the experiments. The flow rate was 1 mL/min and polymer solutions of 0.130 – 3.92 g/L were injected. The increment of refractive index $d\tilde{n}/dC$ for each eluent and molar mass of the polymer were measured on an optical bench fitted with a laser lamp at $\lambda = 633$ nm. The data were treated with the ASTRA 4.1 software.

Viscometric Study

The viscometric measurements were carried out on a SEMATech model Ti.1 viscometer comprising an Ubbelohde type capillary tube of 0.4 mm diameter. The automatic system was thermostated and polymer solutions at concentrations of 2.5 – 20 g/L were used.

RESULTS AND DISCUSSION

Liquid chromatography of polystyrene standards at the exclusion–adsorption transition point was investigated with a series of eluents.

According to the conventional designation, the eluent was composed of one adsorli (hexane) and different desorli (toluene, CH_2Cl_2, THF, EtAc, MEK) in various proportions. A silica column of 100 Å porosity was used as support for these experiments. As already shown in a previous paper, "critical conditions" found for each binary system are obtained at an accurate composition of the eluent and depend very much on the chemical nature of the desorli.[14] As reported in Table I, it appears that the better solvent the desorli is, the lower amount of adsorli (hexane) is necessary to obtain "critical conditions". This result led us to further study the influence of the eluent composition – and specifically, the one obtained at the exclusion–adsorption transition point – on the molecular dimensions of the polystyrene chains. To that purpose, a series of measurements by viscometry and light scattering in solvent mixtures corresponding to the "critical conditions" were undertaken.

Dimension Polymer Chains Under Critical Conditions

The dimensions of the polystyrene chains in desorli/adsorli mixtures of different compositions were measured by means of light scattering and viscometry. This latter technique allows the determination of the Mark–Houwink parameter a through the measurement of the intrinsic viscosity of various polystyrene standards. This parameter gives insight into the permeability of the polymer chains to the solvent flow. By extension, it defines the hydrodynamic polymer/eluent interactions and also "the quality" of the eluent for the corresponding polymer. In such a way, this parameter is suited to express the interactions between the polystyrene chains and the eluent molecules inside the chromatographic column. The light scattering measurements allow the determination of the polystyrene radius of gyration

TABLE I Critical compositions (wt%) of eluents: toluene/hexane, CH_2Cl_2/hexane, THF/hexane, EtAc/hexane and MEK/hexane for polystyrene with $M_w < 10^5$ g/mol. (chromatographic experiments: flow rate of 1 mL/min, $T = 25°C$, UV detection at $\lambda = 261$ nm or refractometric detection, silica column of 100 Å porosity)

	Toluene/ hexane	*CH_2Cl_2/ hexane*	*THF/ hexane*	*EtAc/ hexane*	*MEK/ hexane*
Critical composition (wt%)	83.9/16.1	69.0/31.0	47.0/53.0	37.7/62.3	37.1/62.9

R_g, as well as the second virial coefficient A_2. These data also give insight into the solvation and the molecular dimension of the polystyrene chains and allow us to estimate polymer/eluent interactions.

Viscometric Analysis

The Mark–Houwink parameter *a* was systematically determined for various compositions of the different types of eluent. Its variation is plotted against the hexane content in the eluent, as shown in Figure 2. The dotted vertical lines indicate the respective EATP composition of each eluent.

The variation of *a* with the wt% of hexane (adsorli) in the eluent is strongly dependent on the desorli nature. Indeed, in the cases of toluene and CH_2Cl_2 (best desorli for polystyrene), the Mark–Houwink parameter remains nearly constant within a large range covering the transition from the exclusion to the adsorption modes. This phenomenon can be explained by a preferential solvation of the

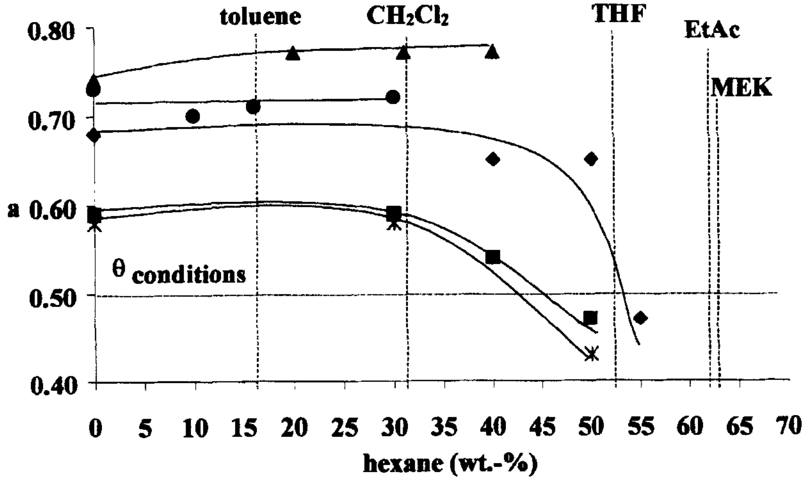


FIGURE 2 Mark–Houwink parameter *a* measured from the viscometry of polystyrene chains *versus* the hexane fraction (wt%) for various desorli/adsorli mixtures: (●) Toluene/hexane, (▲) CH_2Cl_2/hexane, (◆) THF/hexane, (■) EtAc/hexane, (*) MEK/hexane. The dotted vertical lines indicate the chromatographic critical composition in each case (silica column of porosity 100 Å). The dashed horizontal line visualizes the θ-conditions ($a = 0.5$).

polystyrene chains by the desorli as already discussed by Bohdanecky *et al.*[15] Indeed, in a solvent/nonsolvent mixture, the interactions between the molecules of solvent and the polymer chains are dominating and displace the nonsolvent from surrounding the polymer chain. Under these conditions, the permeability of the polymer chains to the flow of the eluent is nearly equivalent to the one of pure solvent.

In the case of poor solvents for polystyrene, *i.e.*, MEK and EtAc, the a parameter decreases when approaching EATP conditions and passes below 0.5 (θ-conditions). It has to be mentioned that the EATP conditions were determined, in these two cases, with polystyrene samples of low molar masses. In the specific case of THF/hexane mixture, a noticeable decrease of a occurs for compositions close to the EATP. Nevertheless, the EATP conditions and θ-conditions could not directly be correlated, *e.g.*, the elution of polystyrene in cyclohexane at 34°C behaves in a adsorption mode and not at the EATP. This study reveals that the critical conditions phenomenon cannot be related to a thermodynamic quality of the eluent. The Mark–Houwink parameter takes different values depending on the nature of the mobile phase. As a consequence, the permeability of the polystyrene chains to the eluent flow, and by extension the hydrodynamic interactions between the polymer chains and the eluent molecules, cannot explain the observed phenomenon.

Light Scattering Analysis

The light scattering study was limited to the best eluents toluene/hexane, CH_2Cl_2/hexane and THF/hexane. The radii of gyration and the second virial coefficients were measured with four polystyrene standards of molar masses higher than 10^5 g/mol in the pure desorli (exclusion mode) and in eluents of critical compositions (EATP). The data given in Table II show that the polystyrene radii of gyration are smaller with THF as desorli as compared with toluene or CH_2Cl_2. This is in agreement with the viscometric study and can be linked to the preferential affinity of the polymer chains towards good solvents.

As noted previously,[14] the polystyrene coils shrink with the addition of hexane in the mixture. Consequently, R_g is smaller in the critical eluent than in the corresponding pure desorli. This size

TABLE II Gyration radii of polystyrene standards (1.35×10^5 g/mol < M_w < 3.22×10^6 g/mol) in pure desorli: toluene, CH_2Cl_2, THF and in the related critical eluents desorli/hexane

		R_g *(nm)*			
	M_w *(g/mol)*	135000	509000	1460000	3220000
Pure desorli	Toluene	15 ± 0.6	33.1 ± 0.7	58.6 ± 0.8	108.1 ± 3.3
	CH_2Cl_2	14.8 ± 0.4	32.1 ± 0.3	57.2 ± 0.2	95.8 ± 0.4
	THF	12.5 ± 1.1	31.3 ± 0.9	57.7 ± 0.5	85.5 ± 0.8
EATP (wt%)	Toluene/hexane 83.9/16.1	13.4 ± 0.6	30.8 ± 0.2	55.4 ± 0.3	97.1 ± 0.8
	CH_2Cl_2/hexane 69/31	13.8 ± 0.3	30.0 ± 0.7	52.2 ± 0.3	89.5 ± 1.2
	THF/hexane 47/53	11.7 ± 0.3	25.4 ± 0.5	38.6 ± 0.3	59.2 ± 0.9

contraction is more pronounced with THF compared to toluene and CH_2Cl_2. Indeed, in the latter cases, the gyration radii are nearly the same, both in the pure desorli and in the respective critical eluents. Figure 3 shows the linear variation of $\log R_g$ *versus* $\log M_w$ for the three critical eluents toluene/hexane, CH_2Cl_2/hexane and THF/hexane. It is worth noting that the slopes differ according to the

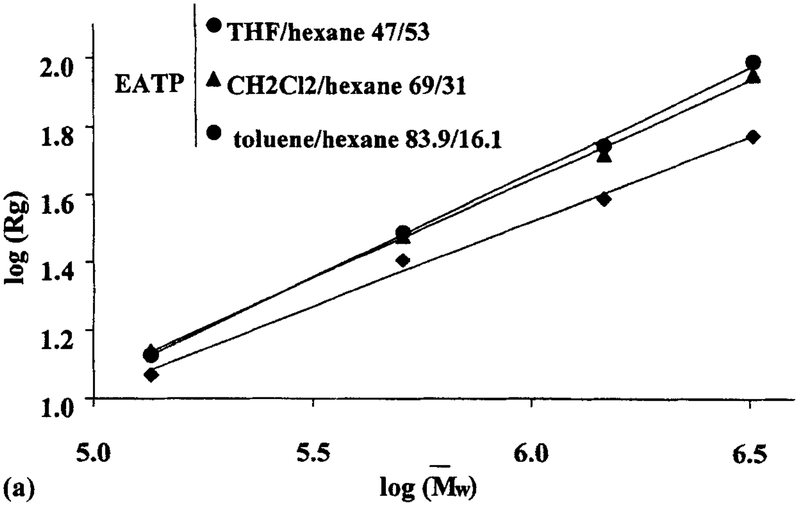


FIGURE 3 Gyration radius *vs.* polystyrene molar mass (1.35×10^5 g/mol < M_w < 3.22×10^6 g/mol) in the critical eluents: (•) Toluene/hexane 83.9/16.1 (wt%); (▲) CH_2Cl_2/hexane 69/31 (wt%); (◆) THF/hexane 47/53 (wt%).

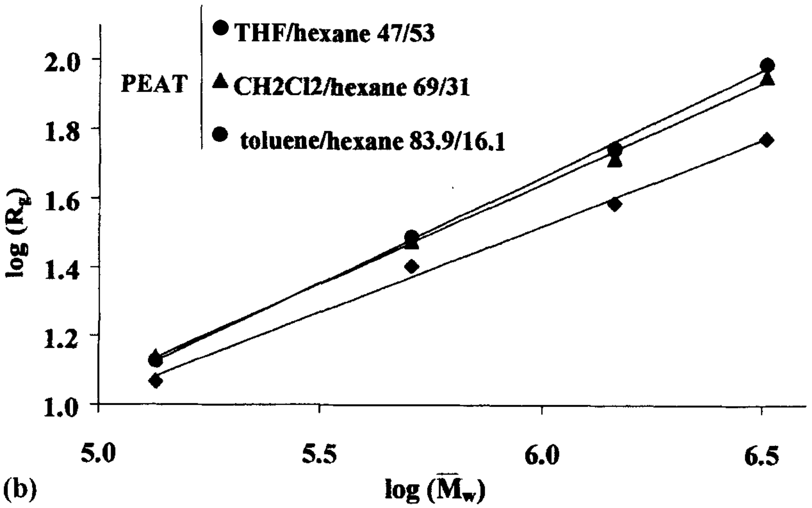


FIGURE 3 (Continued).

nature of the desorli: 0.62 with toluene, 0.58 with CH_2Cl_2 and 0.5 with THF. The comparable behavior in the cases of toluene and CH_2Cl_2 is clearly demonstrated again.

These data show that the changes of the gyration radius as a function of the polystyrene molar mass are different, under the critical conditions, according to the eluent nature. Thus, the EATP phenomenon cannot be linked to a specific molecular conformation of the polystyrene chains in the eluent of critical composition.

The variation of the second virial coefficient A_2 with polystyrene molar mass in the critical eluents as well as in the related pure desorli, is represented in Figures 4a–c. In all cases, the A_2 values are positive, which is a proof of good solvation of the polystyrene chains and also of attractive polystyrene/eluent interactions. Figures 4a–c show also that the transition from the exclusion (pure desorli) to the EATP conditions is accompanied by a decrease of A_2 whatever the nature of the eluent. Indeed, the addition of the adsorli (hexane) diminishes the interactions between the polystyrene chains and the molecules of eluent. This phenomenon is more pronounced in the case of the THF as desorli. In the case of CH_2Cl_2 and toluene as desorli, A_2 remains relatively constant since the EATP conditions are obtained with a lower content of hexane.

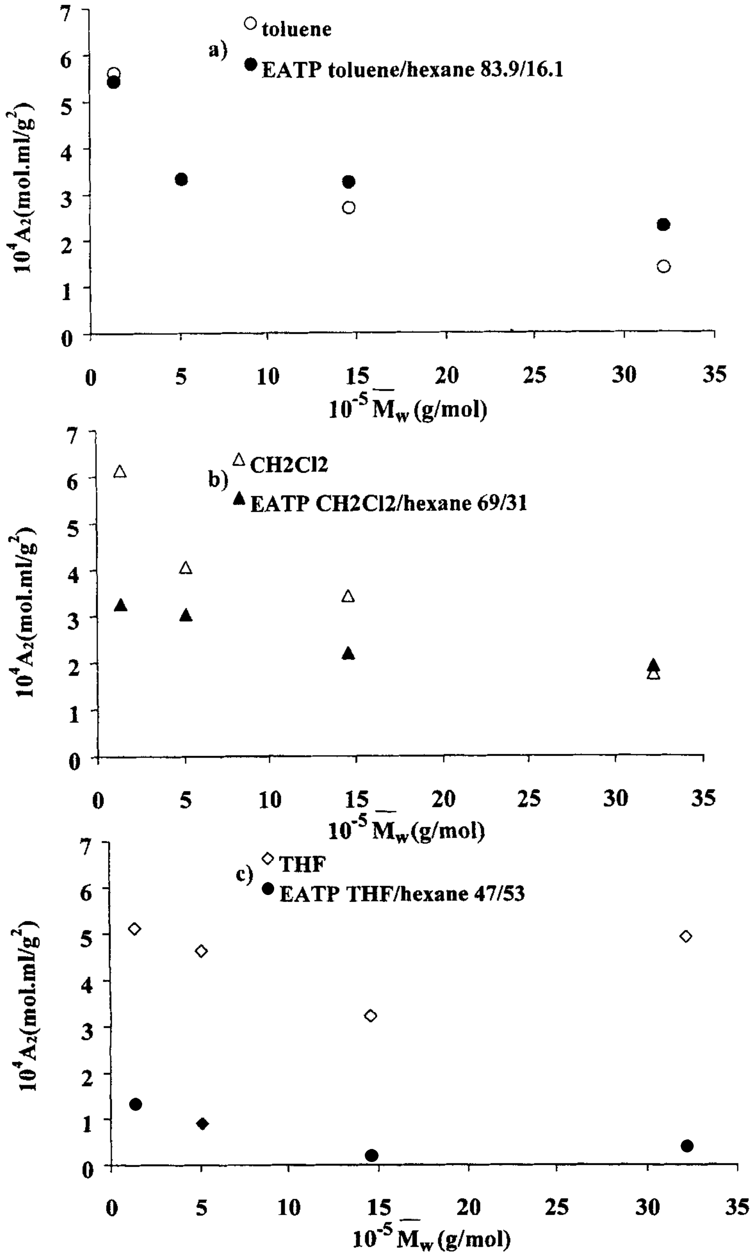


FIGURE 4 The second virial coefficient A_2 *vs.* polystyrene molar mass (1.35×10^5 g/mol $< M_w < 3.22 \times 10^6$ g/mol) in pure desorli and the related critical eluent: (a) Toluene/hexane; (b) CH_2Cl_2/hexane; (c) THF/hexane.

The viscometric and light scattering studies lead to the conclusion that the transition from the exclusion to the EATP modes may be accompanied by the conformational changes of the polystyrene chains. Indeed, the addition of hexane (adsorli) in the eluent usually decreases the polystyrene/eluent interactions (a and A_2 are smaller) and shrinks the polystyrene coils (R_g decreases). Nevertheless, the critical conditions cannot be defined by a specific polymer dimension in the eluent. Indeed, the polystyrene/eluent interactions remain different (a and A_2 are not comparable) and the dimensions of the polystyrene chains (R_g) do not present similar variations with the molar mass.

Adsorbent/Eluent Interactions Under Critical Conditions

The adsorbent/eluent interactions are quantified by the calculation of the eluent strength, ε_0. This parameter is derived from theories developed by Snyder [16] and Soczewinski [17] to explain the adsorption mechanism of organic molecules at the surface of an adsorbent. It defines the free energy of molecules by surface unit under standard activity conditions. A strong interaction between the eluent molecules and the adsorbent surface (high value of ε_0) enables fast elution of the solute. Solvents mostly used in liquid chromatography are classified by increasing order of their strength values.

The eluent strength values of the pure desorli and of the corresponding critical eluents are given in Table III. The addition of hexane in the eluent produces a decrease of the eluent/silica

TABLE III Eluent strengths (ε_0) of the pure desorli: toluene, CH_2Cl_2 and THF and of the related critical eluents: desorli/hexane

Desorli	ε_{0A}[16]	n_b[a]	X_B *(EATP)*[b]	ε_{0AB} *(EATP)*[c]
Toluene	0.22	6.8	0.830	0.21
CH_2Cl_2	0.32	4.1	0.693	0.28
THF	0.53	5.0	0.515	0.47

[a] n_b, the effective molecular area of the respectively desorli. [18]

[b] X_B, molar fraction of the desorli in the critical eluents (chromatographic measurements on silica adsorbent).

[c] An empirical formula [19] has been proposed for the calculation of the eluent strength of a binary mixture, a polar solvent B and a nonpolar one A

$$\varepsilon_{0AB} = \varepsilon_A + \frac{\log\left(X_B 10^{\beta^* n_b(\varepsilon_{0B} - \varepsilon_{0A})} + 1 - X_B\right)}{\beta^* n_b}$$

where ε_{0A} and ε_{0B} are the strength of the respectively pure solvent A and B. β^* defines the activity of the adsorbent. A = hexane, $B \approx$ desorli, $\beta^* = 1$ and ε_0(hexane) = 0.

interactions, since ε_0 is smaller in critical eluent than in pure desorli. Interestingly, it also appears that ε_0 values of each eluent with the same critical composition are not identical. This observation indicates that the interactions between the eluent molecules and the silica surface are not specific in the EATP mode, but depend mainly on the nature of the desorli. As shown in Figure 5, it is worth noting that the higher the desorli/silica interactions (higher ε_0), the higher the content of hexane to obtain the critical composition. Moreover, a linear relationship allows an easy determination of the critical composition.

The above observations show that the transition from the exclusion to the adsorption mode is governed by the competitive interactions between the polystyrene chains and the eluent molecules with the adsorbent surface (silica). The addition of adsorli (hexane) decreases the eluent/adsorbent interactions to the benefit of the polystyrene/adsorbent ones.

Eluent Polarity Under Critical Conditions

The polystyrene/eluent as well as the eluent/adsorbent interactions have a strong influence on the transition from the exclusion to the

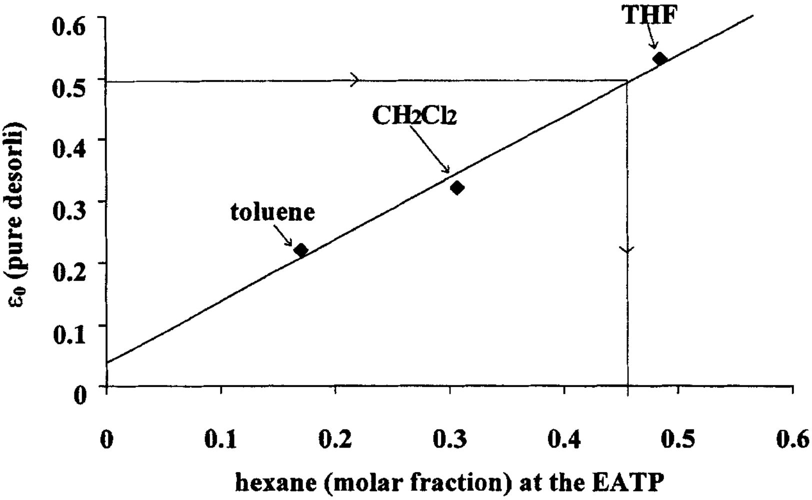


FIGURE 5 Variation of the pure desorli strength (toluene, CH_2Cl_2 and THF) with hexane content in the eluent desorli/hexane of critical composition (polystyrene as solute and silica as adsorbent).

adsorption mode. Nevertheless, they do not clearly explain the influence of the desorli nature on the critical composition of the eluent. This led us to consider the polarity index P' which takes into account all of the interactions. The choice of P' has been discussed in a previous paper.[18] The polarity of an eluent represents its ability to interact by different means (dispersive forces, dipole–dipole interactions, hydrogen bonds, *etc.*) with other molecules. Indeed, this parameter takes into account both the eluent/adsorbent and the eluent/solute interactions. The P' was calculated by Snyder [20] from the experimental measurements of the distribution coefficient of the reference solutes carried out by Rohrschneider,[21] by using gas chromatography. The solutes were chosen to take into account all kinds of interactions that can appear with the solvent molecules. Typically, a solvent which interacts strongly with other molecules has a high value of P'. Rohrschneider also defined a polarity scale from 10^{-1} to 10.

The polarity index of the pure desorli and those of the critical eluents for two types of adsorbent (silica and silica grafted by aminopropyl groups) is given in Table IV. These data confirm that the addition of an adsorli (hexane) decreases the polarity of the eluent, since P' is higher in the pure eluents than in the critical ones. Addition of hexane lowers the interactions of the eluent both with the polystyrene chains and with the adsorbent surface. Table IV also

TABLE IV Polarity index P' of the pure desorli: toluene, CH_2Cl_2, THF and of the related critical eluents desorli/hexane for two adsorbents: silica and silica grafted by aminopropyl groups

		EATP			
	Pure desorli	*Hexane*[a] (*v.*-%)		P'[b]	
Eluent desorli/hexane	P'[20]	*Silica*	*Amino-silica*	*Silica*	*Amino-silica*
Toluene/hexane	2.4	20.1	22.7	1.9	1.9
CH_2Cl_2/hexane	3.1	47.4	49.7	1.7	1.6
THF/hexane	4.0	60.3	49.6	1.7	2.1

[a] Values obtained by chromatographic experiments with polystyrene at 25°C.

[b] P'_{EATP} were determined on a volume fraction basis.

$P'_{EATP} = \phi_{hexane}P'_{hexane} + \phi_{desorli}P'_{desorli}$ with $P'_{hexane} = 0.1$.

reveals that the P' values of the three critical eluents are very close for a given adsorbent. The EATP conditions of a given adsorbent/polymer system seem to be obtained for a "critical polarity" of the eluent, expression of an equilibrium state of the eluent, which interacts both with the adsorbent and the polystyrene chains. The P' value seems also to be a good parameter to evaluate the transition between the exclusion and the adsorption modes in liquid chromatography.

Effect of Temperature

All parameters mentioned above are mostly dependent on the temperature.[22,23] Indeed, the temperature has an influence on the column efficiency and selectivity. It also controls the viscosity of the eluent and consequently the diffusion rate of the solute. A temperature change also modifies the characteristics of the adsorbent, the conformation of the solute as well as the performance of the detectors. The EATP conditions obtained by varying the eluent composition can also be obtained by tuning the temperature, since the latter controls the interaction strength between the solute and the adsorbent.[24] The transition from the exclusion to the adsorption mode *via* the EATP can be carried out by an increase or decrease of the temperature according to the chromatographic system (eluent, adsorbent, solute), since different retention behavior was observed at different temperatures.[25]

Philipsen *et al.*[26] studied the influence of the temperature on the EATP conditions of polystyrene with the eluent CH_2Cl_2/acetonitrile in normal and reversed phases. They found it easier to tune the temperature to refine the EATP conditions instead of varying the eluent composition.

In this paper, we have studied the influence of the temperature on the critical conditions, and on the interactions polymer/eluent and polymer/adsorbent. In this way, the polystyrene was kept as a model and the chromatographic measurements were made with the eluent THF/hexane and the silica column at different temperatures (Figs. 6a–c).

As indicated in Figures 6a–c, a temperature decrease is accompanied by an increase of the polystyrene retention times, whatever the eluent composition. It is worth noting that such an effect can also be obtained by increasing the hexane content in the eluent.

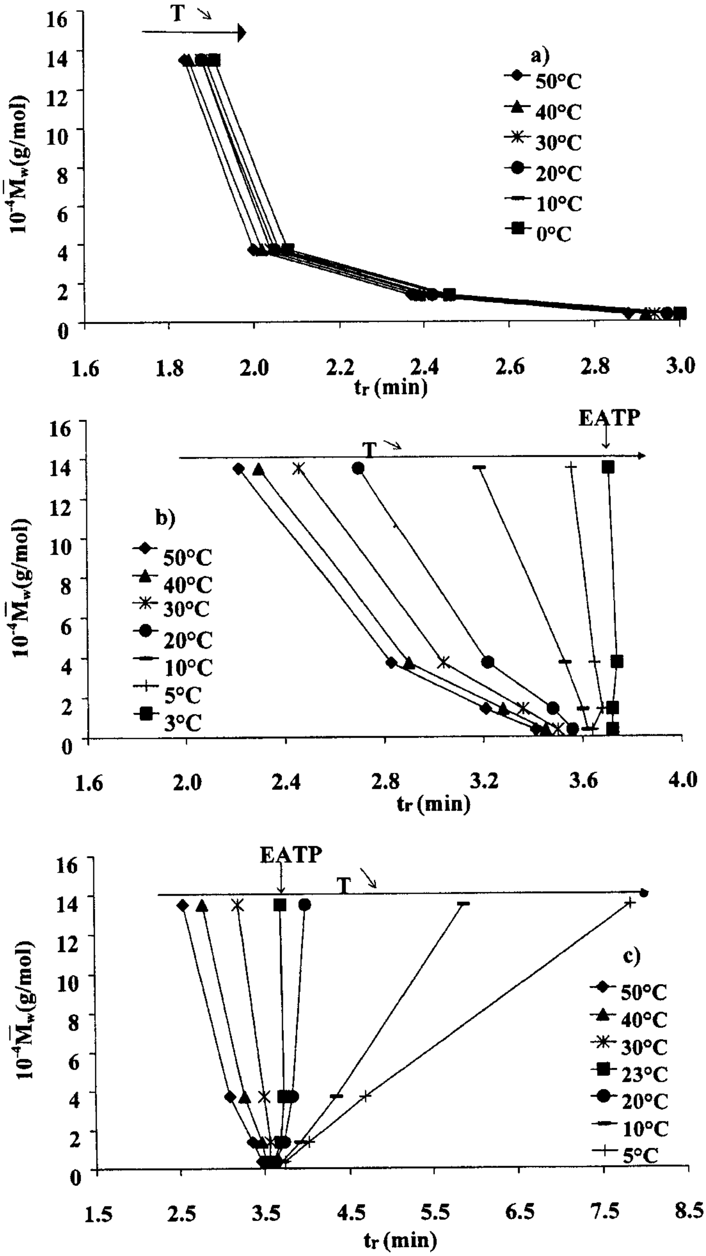


FIGURE 6 Effect of the temperature on the retention times of polystyrene standards (M_w = 3,500, 13,700, 37,000 and 135,000 g/mol) in THF/hexane mixtures (wt%): (a) 100/0, (b) 50/50, (c) 48/52. Nucleosil–silica column (100 Å).

A continuous variation of the polystyrene elution with the composition of the mobile phase is observed. In the case of eluents with less than 50 wt% of hexane, the polystyrene chains are always eluted in an exclusion mode within the temperature range of 0–50°C (Fig. 6a). However, for eluents containing more than 50 wt% of hexane, a decrease of temperature allows the transition from the exclusion to the adsorption mode *via* the EATP (Figs. 6b and 6c). Typically, with the mobile phase THF/hexane 48/52 (wt%) and the silica as adsorbent, three elution modes can be obtained by tuning the temperature. For the temperatures lower than 23°C, the polystyrene chains are eluted in an adsorption mode and above this key temperature, in an exclusion mode. In between these two domains, at 23°C, the polystyrene chains are eluted with the same retention time, known as the EATP mode (Fig. 6c). This specific temperature, T_{EATP}, defines the critical conditions of the polystyrene for the composition 48/52 (wt%) of the mobile phase THF/hexane.

In the case of eluents containing more than 50 wt% of hexane, several EATP temperatures could be found. As illustrated in Figure 7, an increase of 1 wt% of hexane (adsorli) in the eluent requires the temperature to be increased by nearly 10°C to obtain the EATP mode. The EATP temperature increases in a monotonous manner with the

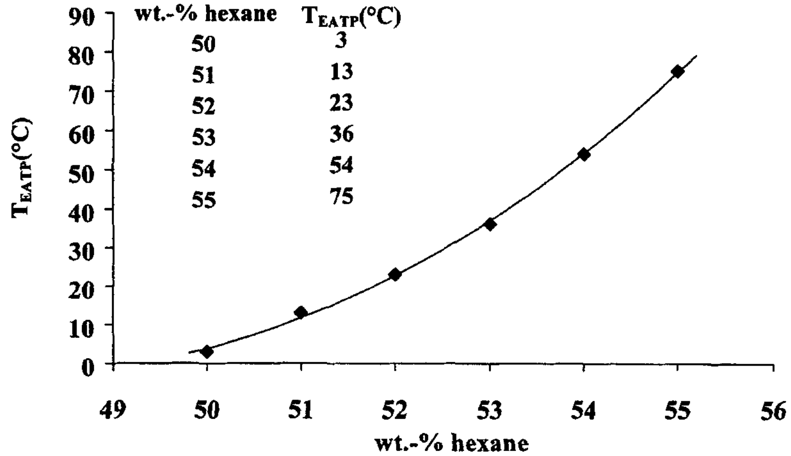


FIGURE 7 EATP temperatures *versus* wt% of hexane in THF/hexane eluent. Nucleosil–silica column. Solute: polystyrene standards.

content of adsorli (hexane) in the mobile phase. Indeed, an increase of the THF (desorli) content or an increase in the temperature has a similar effect on the interactions polystyrene/silica: they favor the polystyrene chains desorption from the silica surface. Consequently, the transition from the exclusion to the adsorption modes will be obtained at a higher temperature for eluent containing more than 50 wt% of hexane (adsorli).

The influence of the temperature on the interactions between the polystyrene chains and the eluent THF/hexane at the EATP conditions was estimated also by viscometric measurements. The Mark–Houwink parameter *a* was measured at 3 different EATP temperatures, see Table V. For comparison, the *a* value for polystyrene in solution in the binary mixture THF/hexane 50/50 (wt%) at 25°C is also reported.

It is particularly important to note that *a* values are identical for three EATP temperatures. This observation underlines the specific interactions between the polystyrene chains and the eluent at the EATP. It is also noticeable that the Mark–Houwink parameter is sensitive to temperature. Typically, for a given composition, 50/50 (wt%) desorli/adsorli, *a* increases from 0.51 to 0.65 with a temperature increase of 22°C. In this way, a temperature increase favor the interactions between the polystyrene chains and the eluent.

To investigate further the temperature effect on the retention, experimental Van't Hoff plots ($\ln K = f(1/T)$) were determined.[27] The Van't Hoff curves allow us to calculate the enthalpy variation ΔH° occurring when a macromolecule passes from the mobile to the stationary phase. A higher value of ΔH° indicates stronger adsorption of the polymer chain onto the surface of the adsorbent. This parameter gives good quantification of the interactions polystyrene/silica in the

TABLE V Mark–Houwink parameter *a* of polystyrene standards in different binary mixtures THF/hexane at the corresponding EATP temperature

Eluent THF/hexane (wt%)	*EATP temperature T_{PTEA} (°C)*	*Mark–Houwink parameter a*
50/50	3°C	0.51
49/51	13°C	0.50
47/53	36°C	0.51
50/50 (25°C)	–	0.65

three chromatographic elution modes: exclusion, adsorption, and critical conditions. The Van't Hoff curves obtained for the polystyrene series and eluted with mobile phases THF/hexane of different compositions are shown in Figures 8a–c.

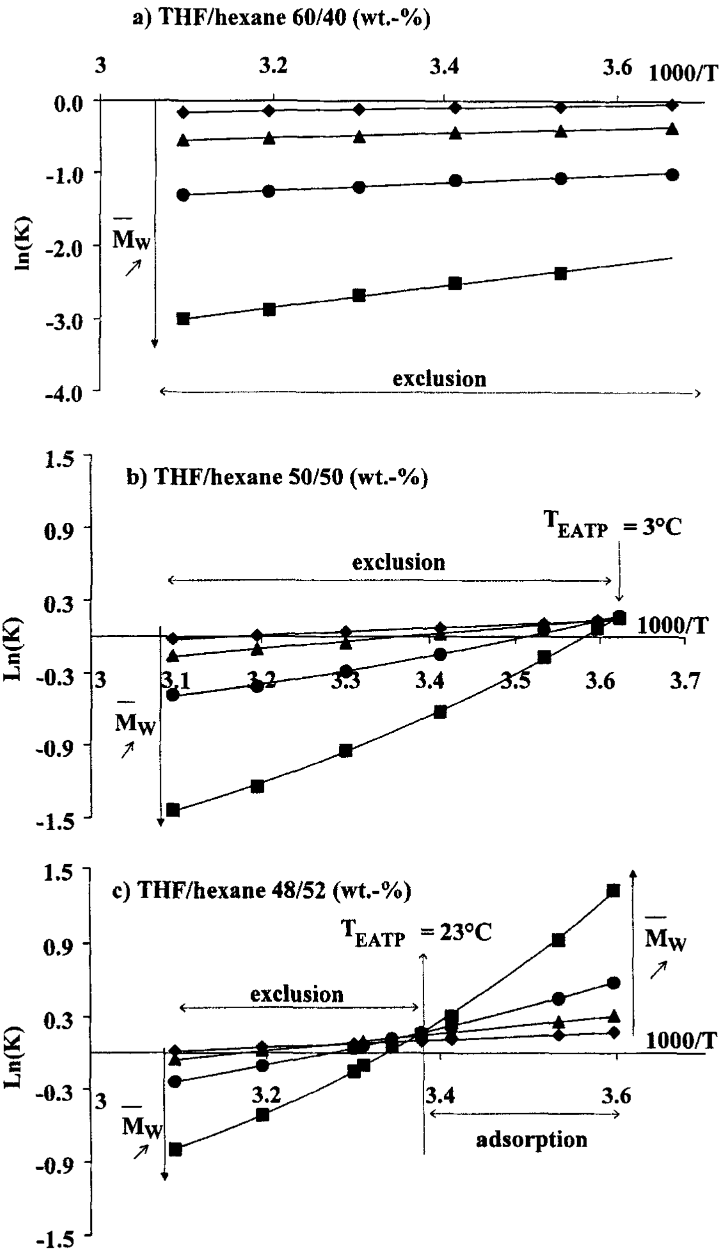
The curves reported in Figures 8a–c, show an increasing and monotonous variation of ln$K$ against the inverse value of the temperature, whatever the mobile phase composition. This is the consequence of the negative ΔH° values due to the exothermic interactions between the polystyrene chains and silica. For smaller molar masses, 3,500 and 13,700 g/mol, ln$K$ is linear *vs.* $1/T$ whatever the mobile phase composition while, for higher molar masses, 37,000 and 135,000 g/mol, different behavior occurs depending on the eluent composition. The Van't Hoff curves remain linear when the mobile phase contains less than 50 wt% of hexane and deviates from the linearity when the mobile phase contains higher proportion of hexane.

In the specific case of the mobile phase THF/hexane 48/52 (wt%), Figure 8c, all the curves $\ln K = f(1/T)$ intersect to a distribution coefficient K independent of the polystyrene molar mass. This point obtained at 23°C defines the EATP phenomenon. For temperatures higher than 23°C, K decreases when the molar mass increases, thus indicating an exclusion mode. Conversely, K increases with the molar mass, in an adsorption mode, for temperatures lower than 23°C. Figures 8a–c confirm that the eluents containing more than 50 wt% of hexane allow the transition from the exclusion to the adsorption mode *via* the EATP in the examined temperature range.

Figure 9 shows the enthalpy variation ($-\Delta H^{\circ}$) with temperature for a series of polystyrenes of different molar masses and with the mobile phase THF/hexane 48/52 (wt%).

As can be seen in Figure 9, $-\Delta H^{\circ}$ decreases with increasing temperature. This effect is only noticeable for polystyrenes with molar masses higher than 37,000 g $\cdot$ mol^{-1}. Moreover, $-\Delta H^{\circ}$ values logically increase with molar mass. The transition from the exclusion to the adsorption mode, *via* the EATP, obtained by decreasing the temperature, can be interpreted by a continuous increase of the interactions between the polystyrene and the silica.

Figure 10 shows the $-\Delta H^{\circ}$ variation *versus* composition of the eluent THF/hexane at 23°C for a series of polystyrenes. It is worth noting that the EATP conditions are obtained, at this temperature, for an eluent composition of 48/52 wt% THF/hexane.


a) THF/hexane 60/40 (wt.-%)

b) THF/hexane 50/50 (wt.-%)

c) THF/hexane 48/52 (wt.-%)

FIGURE 8 Semilogarithmic of the distribution coefficient *vs.* inverse temperature in the case of polystyrene standards (M_w = 3,500 g/mol(◆); 13,700 g/mol(▲); 37,000 g/mol(●); 135,000 g/mol(■)) elution in THF/hexane mixtures (wt%): (a) 60/40, (b) 50/50, (c) 48/52. Nucleosil-silica column (100 Å).

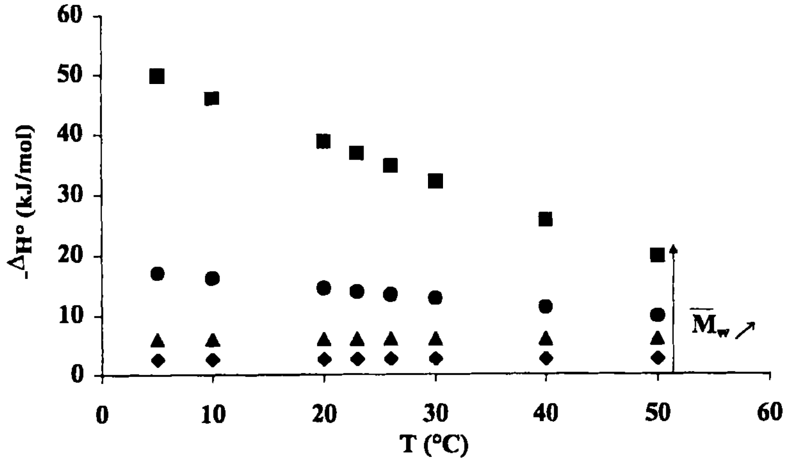


FIGURE 9 Standard enthalpy ($-\Delta H^\circ$) *versus* temperature for a series of polystyrene standards ($M_w = 3{,}500$ g/mol(◆); 13,700 g/mol(▲); 37,000 g/mol(•); 135,000 g/mol(■)) in the eluent THF/hexane 48/52 (wt%). Nucleosil–silica column (100 Å).

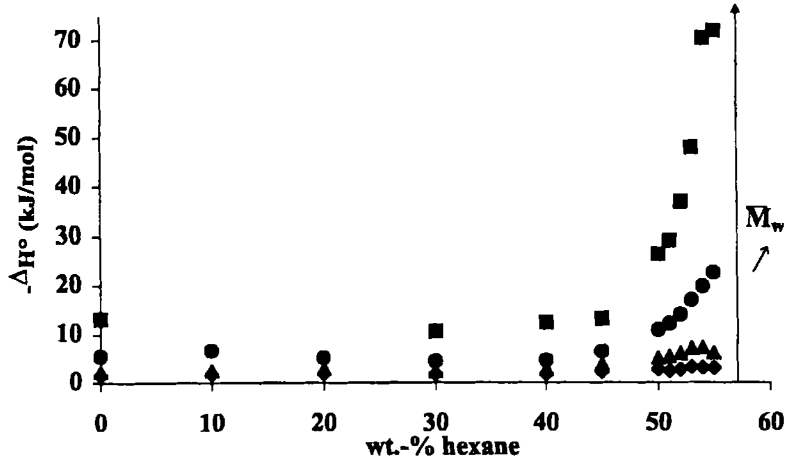


FIGURE 10 Standard enthalpy variation ($-\Delta H^\circ$) *versus* hexane content in the mobile phase THF/hexane for a series of polystyrene standards ($M_w = 3{,}500$ g/mol(◆); 13,700 g/mol(▲); 37,000 g/mol(•); 135,000 g/mol(■)) at 23°C. Nucleosil–silica column (100 Å).

As can be seen in Figure 10, $-\Delta H^\circ$ values increase with the percentage of hexane in the eluent and more particularly for higher molar masses. This demonstrates that the adsorli (hexane) favors the

TABLE VI $-\Delta H^{\circ}$ values for a series of polystyrene standards ($M_w = 3500$, 13,700, 37000 and 135,000 g/mol) at different EATP temperatures, with THF/hexane mixtures as eluents

EATP		$-\Delta H^{\circ}$ *(kJ/mol)*			
wt% of hexane	*EATP temperature (T_{PTEA} in °C)*	*PS* 3500	*PS* 13700	*PS* 37000	*PS* 135000
50	3	2.59	5.01	14.2	34.6
51	13	2.29	5.37	13.7	34.4
52	23	2.55	6.01	13.9	36.8
53	36	3.08	7.11	14.0	34.8
54	54	2.97	7.18	12.3	22.6
55	75	2.88	6.12	8.45	16.4

interactions polystyrene/silica. These interactions remain rather low and constant in the exclusion mode (from 0 to 40 wt% of hexane) and increase strongly when the mobile phase contains more than 50 wt% of hexane.

It was of particular interest to compare the $-\Delta H^{\circ}$ values in different EATP conditions for a series of polystyrenes. As mentioned above, for a given molar mass and a given composition of the eluent, the data collected in Table VI show that the different critical conditions obtained at different temperatures exhibit identical $-\Delta H^{\circ}$ values. This observation indicates that the critical conditions can be defined by specific interactions between the polymer chains and the adsorbent surface. Nevertheless, we note a slight deviation from this assessment for the EATP obtained at elevated temperature. In these cases, we can suppose either a strong variation of the mobile phase viscosity or a possible change in the eluent composition (evaporation).

CONCLUSIONS

The results described in this paper allowed us to better characterize and define the liquid chromatography of polymers at the exclusion–adsorption point. In the exclusion mode, the polymer/adsorbent interactions are low and cannot explain the decrease of retention times when the molar mass increases. This mode is only governed by the size effect of the macromolecules. However, in the adsorption mode, the polymer/adsorbent interactions are proportional to the size of the polymer chain. These interactions govern the retention mechanism and lead to stronger retention time when the molar mass increases. Finally, the transition between these two modes occurs with a progressive increase of the polymer/adsorbent interactions leading to a change of the polymer dimension (R_g, a and A_2 decrease). This transition can be reached by decreasing the temperature or increasing the adsorli content. Critical conditions are obtained for specific values of the polymer/adsorbent interactions, for a given eluent desorli/adsorli and for a "critical polarity" of the eluent.

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[27] Van't Hoff plot and calculation of $\Delta H°$: The distribution coefficient K is linked to the enthalpy variation $\Delta H°$ occurring when a macromolecule transfers from the mobile to the stationary phase, by the relation:

$$\ln K = -\frac{\Delta G°}{RT} = -\frac{\Delta H°}{RT} + \frac{\Delta S°}{R}$$

where $\Delta G°$ and $\Delta S°$ are respectively the free enthalpy and the entropy. R is the gas constant ($R = 8.3145\,\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$) and T the absolute temperature (Kelvin). K was calculated from the chromatographic measurements with the silica column by the relationship:

$$K = \frac{V_e - V_i}{V_p}$$

where V_e is the elution volume, V_i the volume of the exclusion limit and V_p the volume of the pores. V_i was defined as the elution volume of the polystyrene standard of molar mass 135,000 g/mol with the eluent THF at 50°C ($V_i = 1.84$ mL). V_p was calculated as the difference between the total volume of the column V_0 and the volume of the exclusion limit, $V_p = V_0 - V_i$· V_0 was estimated by the elution volume of toluene with the eluent THF at 50°C ($V_0 = 3.44$ mL, and $V_p = 1.60$ mL).

For practical reasons, the temperature range was limited to the interval [0° – 75°C]. The lower value is the limit which can be achieved by the oven and the upper one is given by the vapor tension of the eluent.

$-\Delta H°$ was calculated for linear Van't Hoff plots ($\ln K = f(1/T)$) multiplying the slope by R. If an equation can be obtained for the best fit of a nonlinear Van't Hoff plot, then the partial derivative of $\ln K$ with respect to $1/T$ will yield $-\Delta H°$ divided by R for a given temperature.