



Adsorption thin-layer chromatography and viscometry of polystyrenes in solvent mixtures

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Abstract

The effect of the thermodynamic quality of solvent mixtures on the adsorption behavior of macromolecules under dynamic conditions was investigated. The chromatographic behavior of polystyrenes (PSs) in various mixed eluents was studied under conditions of adsorption and size-exclusion thin-layer chromatography as well as at the exclusion–adsorption transition point with silica gel KSKG adsorbent. The thermodynamic quality of the solvent mixtures used in the chromatographic experiments was determined viscometrically. The dependences of the intrinsic viscosity of PSs on solvent composition for solvent–non-solvent, two solvents, and θ -solvent–solvent mixtures were obtained. A correlation was found between Snyder's polarity indices for the solvent mixtures used in polymer chromatography under “critical conditions” and the intrinsic viscosity values of PSs in the same mixtures.

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1. Introduction

Adsorption liquid chromatography (including thin-layer chromatography) is a unique method for determining the compositional inhomogeneity of polymers [1–10]. It is also applied to determine the molecular mass inhomogeneity of polymers [1,2,10,11]. Adsorption chromatography is also a good tool for studying adsorbate–adsorbent interactions. A peculiar feature of adsorption chromatography is the application of mixed solvents. It is usually a mixture of an adsorption-active solvent

“desorli” and an adsorption-promoting solvent “ad-sorli” [12].

At present, the mechanism of interactive chromatographic techniques is being investigated in detail [13,14]. However, the role of the solvent in the dynamic adsorption of macromolecules is not being given sufficient consideration.

To our knowledge, there are only a limited number of papers that attempt to compare the behavior of macromolecules under conditions of adsorption and critical chromatography with their state in solution, and these draw different conclusions. These are the works of Russian [15,16] and French investigators [17]. The authors of Ref. [17] have investigated the chromatographic behavior of polystyrenes (PSs) in precipitant (hexane)–solvent mixtures (methyl ethyl ketone, ethyl acetate, tetrahy-

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drofuran and CH_2Cl_2) and have come to the conclusion that critical adsorption conditions are always attained at similar values of Snyder's polarity indices. It has been shown in Ref. [15] that, to attain the same values of the retention factor of macromolecules, the better the thermodynamic quality of the eluent for the investigated polymer, the higher should be its polarity index.

Therefore, the problem of the effect of the thermodynamic quality of the solvent on the adsorption behavior of macromolecules under dynamic conditions remains unsolved.

2. Experimental

2.1. Polymers

The polymers used in the investigation were PSs of $M_w \cdot 10^{-3}$ 1.4, 5.0, 30, 40, and 460 synthesized by anionic polymerization at the Institute of Macromolecular Compounds, and of narrow molar mass (MM) distribution ($M_w/M_n < 1.1$, where M_w is the weight-average molar mass and M_n is the number-average molar mass), and PS standards from Waters.

2.2. Solvents

Cyclohexane (Merck, Darmstadt, Germany), spectrophotometric grade, and hexane (Novocherkassk, Russia), spectrophotometric grade, were used as received. Carbon tetrachloride and toluene, both analytical grade (Reactive, Saint-Petersburg, Russia), and methyl ethyl ketone (MEK) (Reanal, Budapest, Hungary), analytical grade, were distilled prior to use. Tetrahydrofuran (THF) (Reactive), analytical grade, was distilled over sodium hydroxide before use. All solvent mixtures for chromatography were specified as volume ratios. Mark–Kuhn–Houwink parameters (K and α) for PSs [18] and Snyder's parameters (P') for neat solvents [19] are presented in Table 1.

2.3. Conditions

Chromatography was performed on "Sorbfil" (Sorbpolymer, Krasnodar, Russia) 10 cm × 10 cm aluminium-foil-backed HPTLC plates precoated with

Table 1
Mark–Kuhn–Houwink parameters (K and α) and Snyder's parameters (P') for neat solvents

Solvent	Mark–Kuhn–Houwink parameter			P' ^a
	α^b	$K \cdot (10^3)^b$ (ml/g)	T (°C)	
MEK	0.58	39	25	4.7
	0.635	19.5	25	
	0.6	30.5	25	
THF	0.713	12.5	25	4.0
Toluene	0.71	13.4	25	2.4
CCl_4	0.7	15	25	1.6
Cyclohexane	0.5	82	34	0.2
	0.5	84.6	34.5	

^a See Ref. [19].

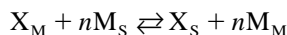
^b See Ref. [18].

silica gel KSKG (pore diameter 110 Å) with a fluorescent indicator. After plate activation by heating at 105 °C for 30 min, PS solutions in CCl_4 (0.5–5.0 mg ml⁻¹) were spotted with a 1 µl calibrated capillary (Camag, Switzerland) at a distance of 1 cm from the plate edge. Ascending one-dimensional single development to a distance of 8 cm was performed in S-type and N-type saturated and unsaturated chambers (for 10 × 10 cm plates; Sorbopolymer) using binary and ternary solvent mixtures (10 ml) at 20 °C. PS spots were detected under a UV₂₅₄ lamp or by carbonization as described elsewhere [20]. R_f measurements were made at least in triplicate. The average reproducibility of R_f values (S_r) was better than 5%. The relative humidity was 56%.

An Ubbelohde capillary viscometer was used for intrinsic viscosity ($[\eta]$) determinations with a solvent efflux time of about 100 s at 25 and 35 °C. The temperature was controlled to within ±0.05 °C of the stated value. PSs were dissolved separately in solvent mixtures, prepared by the direct mixing of the initial components in different proportions. Mixture composition is given in weight fractions. Polymer concentrations were calculated in volume percent. At least five flow times were recorded for each polymer solution. The experimental points of reduced viscosity versus concentration were on a straight line, which was extrapolated to zero concentration to obtain the intrinsic viscosity value.

3. Results and discussion

In the liquid adsorption chromatography of small molecules, the retention of a solute molecule is determined by the competing interaction between the solvent (M) and the sample molecules (X) for active adsorbent centers (S) [21–24]:



The following types of interactions occur in adsorption chromatography.

(1) The interaction between the adsorptive (X) and the adsorbent (S), i.e. the transition from solution volume (X_M) on the adsorbent surface (X_S): $X_M + S \rightleftharpoons X_S$. This interaction is characterized by free energy E_{X_S} [24].

(2) The interaction of solvent molecules (M) with the active centers of the adsorbent (S), $M_M + S \rightleftharpoons M_S$, which is characterized by free energy E_{M_S} . The chromatographic activity of the solvent may be estimated, for instance, with the aid of Snyder's parameters (P') [19,25]. The strength of the solvent mixture may be evaluated on the basis of Snyder's polarity indices and the volume fraction of the components [26–28] according to the equation $P' = \sum P'_i \phi_i$.

(3) The adsorptive also interacts with the mobile phase. However, for small molecules, interactions in solution are not taken into account, therefore $E_{X_S} \approx nE_{M_S}$ for distribution coefficient $K_d = 1$ [24].

In contrast, for polymers a change in the thermodynamic quality of the solvent leads to a change in the balance between intramolecular interactions and polymer–solvent interactions. Correspondingly, the hydrodynamic volume of the macromolecule and the intrinsic viscosity ($[\eta]$) also change. Hence, if the macromolecule plays the role of an adsorptive, the necessity arises to study the peculiarities of the adsorption behavior of the macromolecule using its chromatographic and hydrodynamic characteristics.

It should be noted that, in theory [29–31], only the parameter of the macromolecular interaction with the adsorbent is taken into account.

To solve this problem, we analyzed the literature data and also investigated the adsorption behavior of PS samples in eluents that were mixtures of solvents with different adsorption abilities, “adsorli” and

“desorli” (Tables 2 and 3). Further PS behavior was compared under conditions of adsorption and size-exclusion chromatography as well as under critical adsorption conditions. Viscometric data were also applied.

3.1. Determination of intrinsic viscosity of PS in solvent mixtures

The thermodynamic quality of the solvent mixture was evaluated by viscometry. The dependences of PS intrinsic viscosity ($[\eta]$) on solvent mixture composition were obtained for the following mixtures: good solvent–precipitant, two good solvents, and θ -solvent–good solvent. The determination of $[\eta]$ for PSs in neat solvents is a trivial task. The values of $[\eta]$ can be readily calculated from the known values of the Mark–Kuhn–Houwink constants K and α : $[\eta] = KM_v^\alpha$, where M_v is the viscosity-average molecular weight.

The determination of $[\eta]$ for solvent mixtures is more complex. The value of $[\eta]$ for a solvent mixture cannot be calculated as an additive sum of the products of the $[\eta]$ values in an individual solvent by the volume fraction of the solvent. This calculation is correct only in the absence of specific interactions: polymer–solvent and solvent components forming a mixture.

The $[\eta]$ value was measured for PSs of M_w $460 \cdot 10^3$ in toluene, MEK, THF, CCl_4 , and their mixtures with cyclohexane as well as in neat cyclohexane. For a mixture of two good solvents (toluene– CCl_4), a linear dependence of $[\eta]$ on mixture composition was obtained. In this case the $[\eta]$ value of the polymer corresponds to its additive value and can always be calculated. In solvent–precipitant mixtures, the values of $[\eta]$ virtually do not change up to the beginning of polymer precipitation, which corresponds to the literature data [17]. This shows that, in solvent–precipitant systems over a wide concentration range, the hydrodynamic volume of the macromolecule corresponds to that in the solvents. As will be shown below, this conclusion is also confirmed by chromatographic data.

In θ -solvent–good solvent mixtures, which include mixtures of cyclohexane with toluene and THF, the dependences of $[\eta]$ on composition are nonlinear. The dependence for the cyclohexane–THF mixture is

Table 2
Chromatographic conditions and characteristics of binary solvent mixtures

Eluent	Chamber type	Snyder's parameter for binary solvent mixtures of the following compositions ($\phi_1 \cdot 10^2 / \phi_2 \cdot 10^2$)																	MM ($\cdot 10^{-3}$) of PS	
		5:95	10:90	15:85	20:80	25:75	30:70	35:65	40:60	45:55	50:50	55:45	60:40	65:35	70:30	75:25	80:20	85:15		90:10
Toluene-CCl ₄	Saturated	1.68		1.76		1.84		1.92		2.00		2.08	2.12	<i>2.16</i>		<i>2.24</i>				1.4–800
	Unsaturated	1.68		1.76		1.84		1.92		2.00		2.08		2.16		<i>2.24</i>				1.4–800
	S-chamber							1.92	1.96	2.00	2.04	2.08				<i>2.24</i>				1.4–800
MEK-cyclohexane	Saturated	0.65	0.88	1.10																1.4–800
	Unsaturated	0.65	0.88	1.10	1.32															1.4–800
	S-chamber		0.88	1.10																1.4–800
THF-cyclohexane	Saturated		0.77	0.96		1.34		1.72												1.4–800
Toluene-cyclohexane	Unsaturated														1.85	1.96	2.07			117–460
Toluene-hexane	Saturated					0.79		1.02		1.25		1.48		1.71		<i>1.94</i>				0.48–800
	Unsaturated					0.79		1.02		1.25		1.48		1.71	1.82	<i>1.94</i>	<i>2.06</i>	<i>2.17</i>		0.48–800
MEK-hexane	Saturated	0.33	0.56		1.02		1.48	1.71	1.94		<i>2.40</i>									0.48–40
	Unsaturated	0.33	0.56	0.79	1.02		1.48	1.71	<i>1.94</i>		<i>2.40</i>									0.48–40

Adsorption mode in normal typeface, “critical conditions” mode in bold and size-exclusion mode in italics.

Table 3
Characteristics and chromatographic conditions for cyclohexane–toluene–MEK mixtures

Composition of cyclohexane–toluene–MEK mixture (v/v)	Chamber type	Mode of chromatography	$[\eta]$ (dl g ⁻¹ for PS of $M_w \cdot 10^{-3} = 460$)	P'
83:10:7	Saturated	Adsorption	0.78	0.74
83:10:7	Unsaturated	Adsorption	0.78	0.74
83:10:7	S-chamber	Adsorption	0.78	0.74
80:13:7	Unsaturated	Adsorption	0.79	0.80
81:10:9	Unsaturated	“Critical conditions”	0.80	0.82

shown in Fig. 1. For the cyclohexane–MEK mixture, a dependence with a maximum is obtained (Fig. 2). Moreover, both the value of $[\eta]$ and the maximum position depend only slightly on temperature in the range from 25 to 35 °C.

These type dependences are described in the literature. It is known [32,33] that, sometimes, two thermodynamically “poor” solvents form a mixture which exhibits high dissolving ability with respect to the polymer, in other words a synergetic effect appears. It is expressed in the formation of a maximum on the curves of solubility, intrinsic viscosity, and the second virial coefficient [34]. Sometimes, the inverse effect is also observed for

thermodynamically “good” solvents. Although many such facts have been reported in the literature, they have not been satisfactorily explained.

In the light of modern concepts of solution theory [35], the most probable explanation is preferential solvation, leading both to a change in solvent composition and the solvate shell and to a change in the interaction between the solvent molecules in the solvate shell as compared to their interaction in the solvent itself. This effect is determined by the balance of polymer–solvent and solvent–solvent interactions. Viscometric results give a hint of the great complexity of the interactions in ternary polymer systems (polymer in a binary solvent).

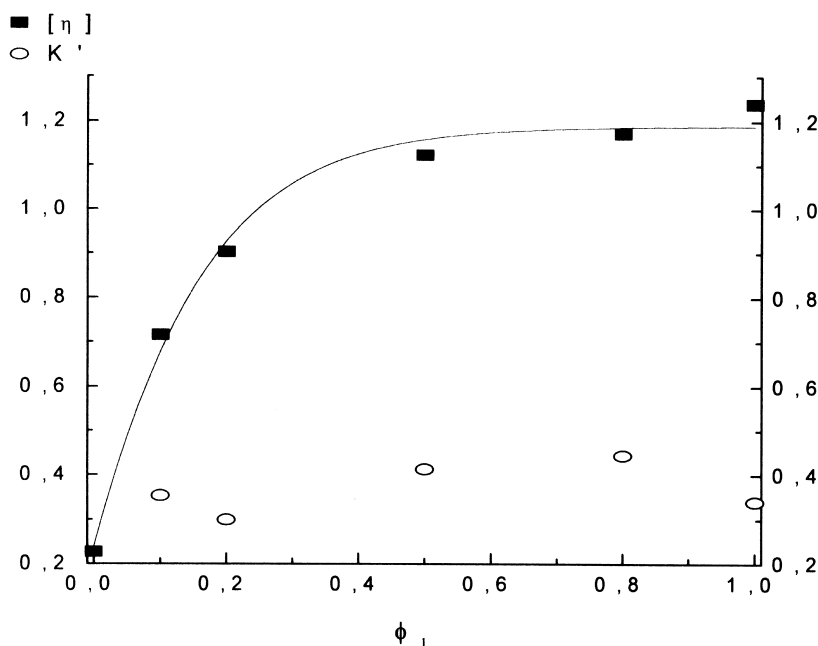


Fig. 1. Intrinsic viscosities ($[\eta]$) and Huggins constants (K') of PS of $M_w \cdot 10^3 = 460$ in THF–cyclohexane; ϕ_1 is the volume fraction of THF.

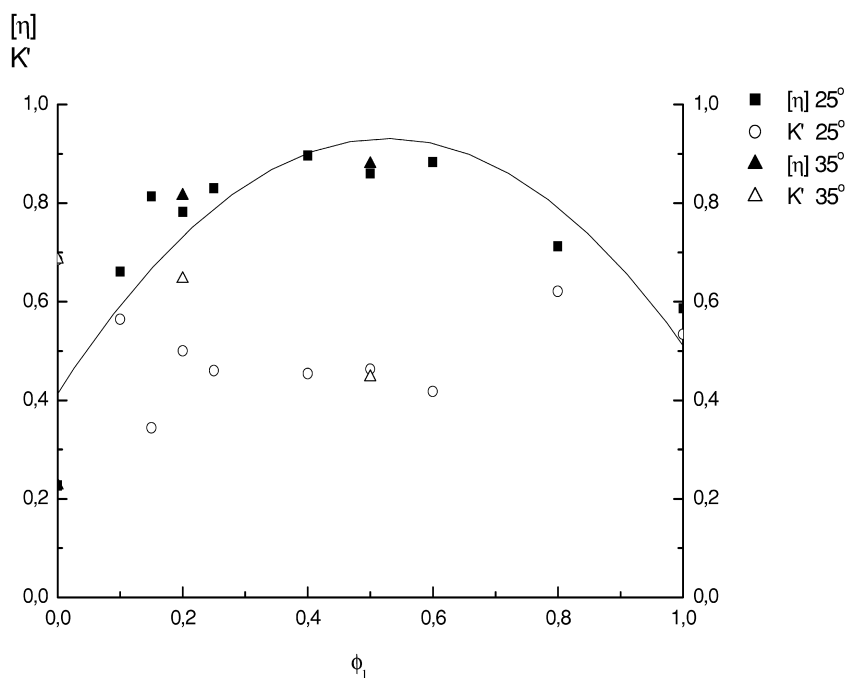


Fig. 2. Intrinsic viscosities and Huggins constants of PS of $M_w 460 \cdot 10^3$ in MEK–cyclohexane; ϕ_1 is the volume fraction of MEK.

3.2. Chromatography of PSs

It is known that two types of mobile phase compositions are used to separate PSs according to molecular mass in the adsorption mode of TLC [10]. One of them, a three-component composition, is a mixture of cyclohexane, benzene, and acetone (or a similar mixture of cyclohexane, toluene, and MEK). It is possible to separate styrene oligomers and PSs with MMs up to $1800 \cdot 10^3$ with the aid of this mobile phase. The second type of mobile phase consists of two components: cyclohexane–toluene or cyclohexane–benzene. This mixture enables the separation of PSs up to $500 \cdot 10^3$. Calculation of the mobile phase strength on the basis of Snyder's polarity indices (P') [26–28] and volume fractions of components (ϕ_i) showed that the strength of a two-component mixture is much greater than that of a three-component mixture [15,16].

In agreement with the viscometric data, which make it possible to evaluate the mean-square radii of macromolecules, the thermodynamic quality of the first type is inferior to that of the second type of mixture. Consequently, with the first type of mobile

phase, the macromolecules have a smaller hydrodynamic volume, and for PS desorption it is sufficient to use a mobile phase of relatively low polarity. With the second type of mobile phase, the macromolecules occupy a greater hydrodynamic volume and, hence, a more polar mobile phase is necessary to carry out adsorption chromatography. Macromolecules characterized by a greater hydrodynamic volume in the mobile phase probably have a greater number of contacts with the adsorbent surface than those occupying a smaller hydrodynamic volume [15].

In the present work, new experimental facts are reported confirming the effect of the thermodynamic quality of the binary solvent mixtures used as mobile phase on the behavior of linear PSs. The chromatographic behavior of PSs in mixtures of solvents characterized by different Snyder's polarity indices was compared. Solvent mixtures were selected in such a way so as to establish the effect of the hydrodynamic volume of the macromolecules on their chromatographic behavior. The characteristics of the eluents for adsorption, size-exclusion and the critical modes of chromatography are given in Tables

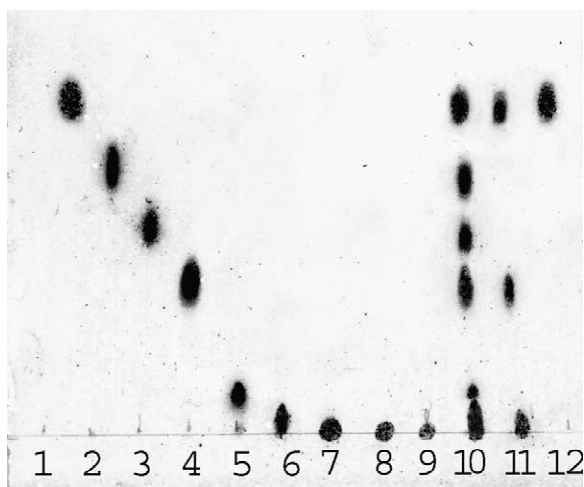


Fig. 3. Chromatogram of PSs with M_w ($\cdot 10^{-3}$) of (1, 12) 2.1, (2) 10, (3) 20.8, (4) 33, (5) 111, (6) 200, (7) 498, (8) 867 and (9) 2600 and their mixtures (10, 11) obtained by step-wise elution to a distance of 4 and 8 cm in a saturated chamber using a THF–cyclohexane (20:80) mixture as eluent.

2 and 3. The investigations were carried out in saturated, unsaturated and S-chambers. The values of Snyder's parameters were calculated by the above-

described method. The separation of PSs in a saturated N-chamber using a THF–cyclohexane mixture as eluent is shown in Fig. 3.

The dependences of the retardation factor R_f on the mobile phase composition for PSs of different molecular masses are shown in Figs. 4–6. These figures show that the R_f values increase with decreasing content of the less polar component CCl_4 (as well as cyclohexane, or hexane) in the solvent. In an unsaturated chamber and in an S-chamber (Figs. 4 and 6), the R_f values increase for all PSs with increasing eluent polarity up to $R_f = 1$. The greater the MM of the polymer, the lower the R_f value of the corresponding chromatographic zone, regardless of eluent composition.

In an unsaturated chamber, the eluent front migration velocity depends on the pore volume of the sorbent [36]. This velocity is slower than the linear eluent velocity behind the front because of eluent consumption by filling of the pores. This phenomenon hinders macromolecule separation according to MM in the adsorptionless regime [20] and causes polymer concentration near the front. In a saturated chamber, pore filling takes place because of the adsorption and capillary condensation of eluent

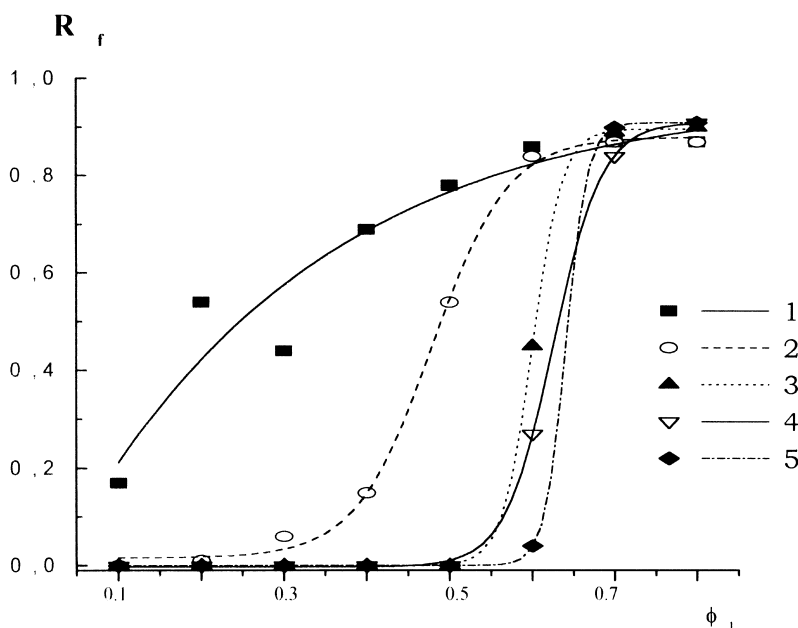


Fig. 4. R_f values for PSs of M_w ($\cdot 10^{-3}$) (1) 1.4, (2) 5.0, (3) 20.8, (4) 30 and (5) 40 obtained by chromatography in an unsaturated chamber using a toluene– CCl_4 mixture as eluent; ϕ_1 is the volume fraction of toluene.

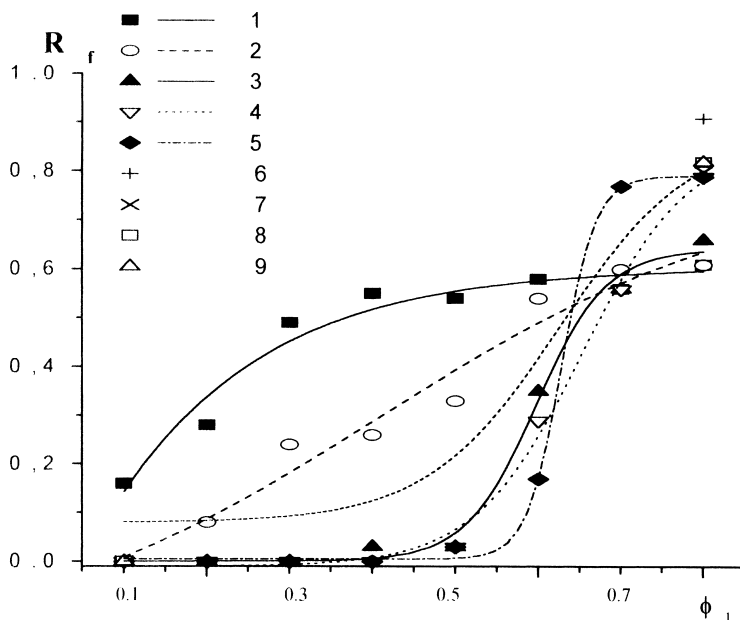


Fig. 5. R_f values for PSs of $M_w \cdot 10^{-3}$ (1) 1.4, (2) 5.0, (3) 20.8, (4) 30, (5) 40, (6) 111, (7) 200, (8) 498 and (9) 867 obtained by chromatography in a saturated chamber using a toluene- CCl_4 mixture as eluent; ϕ_1 is the volume fraction of toluene.

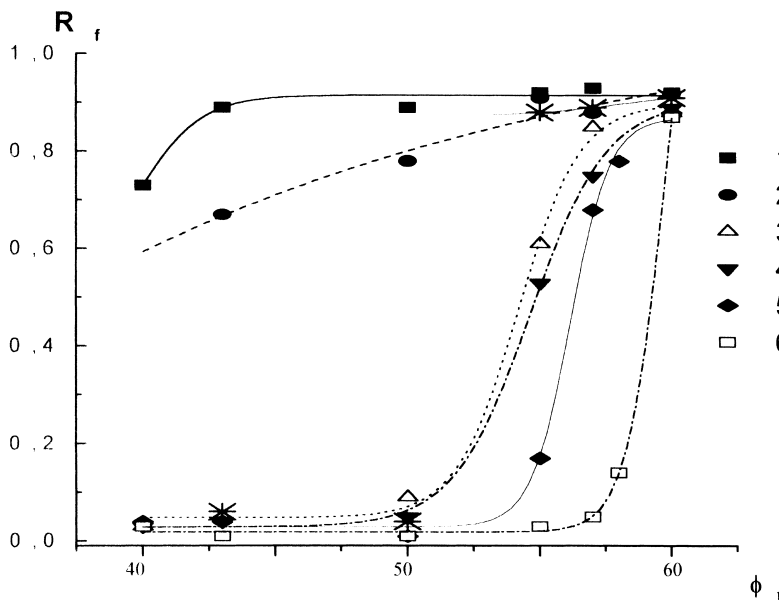


Fig. 6. R_f values for PSs of $M_w \cdot 10^{-3}$ (1) 1.4, (2) 5.0, (3) 20.0, (4) 30, (5) 40 and (6) 111 obtained by chromatography in an S-chamber using a toluene- CCl_4 mixture as eluent; ϕ_1 is the volume fraction of toluene.

components in adsorbent pores, and, therefore, elution proceeds under conditions similar to those in column chromatography.

The “ R_f –eluent composition” (Fig. 5) dependence clearly shows the adsorption and the size-exclusion regions as well as the critical region characterized by the absence of R_f dependence on the polymer MM. In the adsorption region, the R_f values decrease with increasing polymer MM. In the size-exclusion region, i.e. at high concentration of adsorption-active solvent (desorli), the opposite dependence for PSs with different MM is observed.

As follows from Figs. 4–6, the R_f dependences on eluent composition in saturated, unsaturated, and S-chambers do not coincide. In the S-chamber (Fig. 6) the vapor phase is absent and, therefore, the possibility of solvent vapor adsorption is also absent. In the saturated chamber, adsorption processes are so intensive that the size-exclusion mechanism is observed for sufficiently polar eluents at long chromatography times. In the unsaturated chamber, modification of the dry adsorbent by solvent vapor is also

observed, but to a much smaller extent than in the saturated chamber. Hence, the difference in polymer R_f values in different chamber types can be explained by the different adsorption of the eluent components by the dry adsorbent layers. This leads to a difference between the initial and effective eluent compositions. Fig. 7 shows R_f values as functions of PS MM in binary solvent mixtures with similar strengths but different thermodynamic properties. High retention (lower R_f values for PS with the same MM) is observed for mixtures having a better thermodynamic quality.

Of note are the considerable differences between critical eluent compositions and eluent strengths for MEK–hexane (precipitant for PS) and MEK–cyclohexane (θ -solvent for PS), as shown in Table 2. This can be explained by the difference in the solvate shell composition for mixtures containing either precipitant or a θ -solvent. Probably, for MEK–hexane mixtures, the solvate shells are depleted of hexane in comparison with the volume of the solvent mixture of any composition.

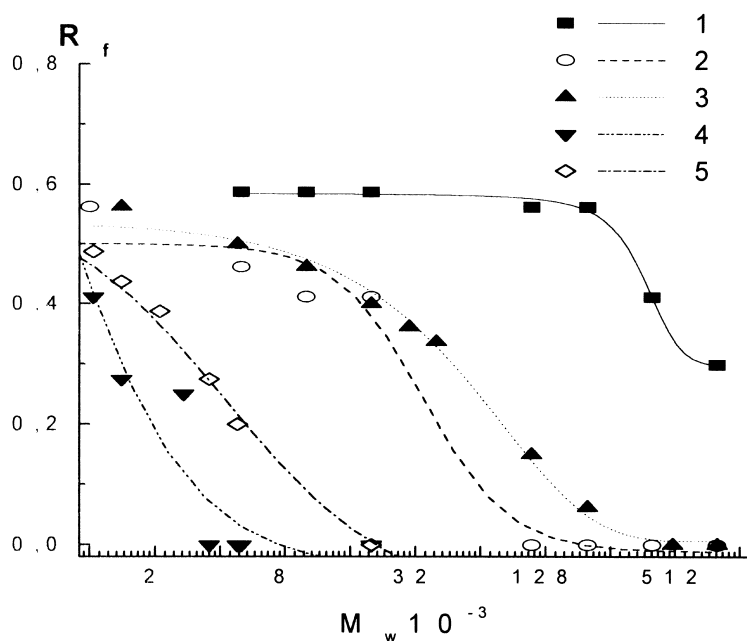


Fig. 7. R_f values for PSs with $M_w (\cdot 10^{-3})$ 1.4–867 in a saturated chamber obtained by chromatography in solvent mixtures (ϕ_1/ϕ_2): (1) MEK–cyclohexane (15:85), (2) THF–cyclohexane (15:85), (3) THF–cyclohexane (20:80), (4) toluene–hexane (40:60), (5) MEK–hexane (20:80).

3.3. Effect of thermodynamic quality of the eluent on PS chromatographic behavior

To evaluate the influence of the thermodynamic quality of the solvent, the dependences of R_f on eluent composition were determined. The eluent composition (or the composition range) for which the transition from the adsorption to the size-exclusion

separation mechanism is observed was then determined. Fig. 8 shows the dependences of P' on $[\eta]$ for PS with $M_w 460 \cdot 10^3$. As can be seen from the plot, an increase in $[\eta]$ is accompanied by an increase in P' . Consequently, in adsorption chromatography, as in size-exclusion chromatography, retention values depend on the hydrodynamic volume of the macromolecule. It is this that explains the

Linear Regression:

$$Y = A + B * X$$

Parameter	Value	Error
A	-1,14626	0,23166
B	2,81057	0,23257

R	SD	N	P
0,97369	0,12225	10	<0,0001

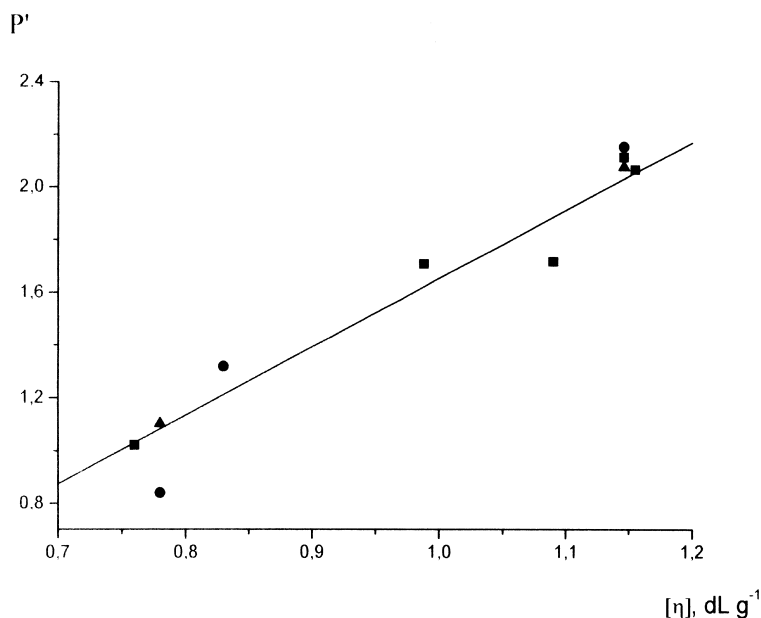


Fig. 8. Correlation between Snyder's parameters (P') and intrinsic viscosities ($[\eta]$) obtained for PS with $M_w 460 \cdot 10^3$ in binary and ternary solvent mixtures, corresponding to "critical conditions" of adsorption chromatography.

complexity of eluent selection in polymer separations according to MM under conditions of adsorption chromatography.

In other words, for the same eluent P' values the retention is greater in those eluents in which the hydrodynamic volume of the macromolecules is greater. This conclusion is also supported by the data presented in Fig. 7. The dependences of R_f on the MM of PS obtained in cyclohexane–MEK eluent are located higher (i.e. retention is weaker) than those obtained in cyclohexane–THF at similar values of P' for these eluents.

As a rule, adsorption chromatography is carried out in solvent mixtures. Under these conditions, an additional degree of freedom appears for polymers: the change in the hydrodynamic volume of the macromolecules. When the eluent composition changes, two parameters are usually changed simultaneously: the strength of single contacts of the macromolecule with the adsorbent surface and the number of these contacts. Hence, in a poor thermodynamic quality eluent the macromolecules have a small hydrodynamic volume and for their desorption a solvent mixture with relatively low polarity is sufficient. In a good thermodynamic quality eluent, the macromolecules have a large volume, and for chromatography under the adsorption regime a more polar solvent is required. For any type of eluent it is possible to pass from the adsorption to the critical mode of chromatography and then to adsorptionless conditions by slightly changing the mobile phase composition, i.e. by slightly changing the strength and thermodynamic quality of the solvent.

For critical conditions the following equation is obeyed [2]:

$$-\varepsilon_i N_i = T \Delta S_i \quad (4)$$

where ΔS is the change in entropy when the macromolecule enters a pore and $-\varepsilon$ is the energy of interaction of a polymer segment with the sorbent surface. For polymers, we have $-\Delta H = -\varepsilon N$, where ΔH is the change in enthalpy, and N the number of segments in the macromolecule.

This means that, at least under critical conditions for extreme values of $[\eta]$ (see Fig. 8, P' vs. $[\eta]$), $-\varepsilon_{\text{good}} N_{\text{good}}$ is almost three times greater than $-\varepsilon_{\text{poor}} N_{\text{poor}}$. There may be only two reasons for this

difference in the $-\varepsilon N$ values and, correspondingly, in solvent strength at similar values of the retention factor.

The first reason is the different values of the interaction energy of the polymer segment ($-\varepsilon$) with the adsorbent surface. The second reason is the different numbers of contacts of the polymer chain with the surface in the above mixtures for the same values of MM and retention factors. With respect to the first reason, the existence of two enthalpy values would mainly lead to the existence for oligostyrenes of two types of mobile phase with considerably different strengths. Attempts to detect such eluents for oligostyrenes failed (see Ref. [2] for eluent compositions). For these, the solvent strength on passing from adsorption to adsorptionless conditions and also when using different eluents is actually independent of mobile phase composition. Hence, the enthalpy of a known segment interaction with the surface cannot change two or three times when the mobile phase composition changes.

Consequently, the second suggestion is correct: the macromolecule that is more uncoiled in the eluent also remains more uncoiled when adsorbed in a pore. In other words, the number of contacts of the macromolecules with the surface is greater in chromatography with an eluent of good thermodynamic quality. If the macromolecule is uncoiled during adsorption and located on the surface in such a way that adsorbed parts alternate with loops (loops and trains model), the loop size and the thickness of the adsorbed layer increase when the eluent quality becomes inferior.

4. Conclusions

To investigate the effect of the thermodynamic quality of solvent mixtures on the adsorption behavior of macromolecules, thin-layer chromatography of polystyrenes was undertaken in the adsorption and size-exclusion chromatographic modes as well as at the exclusion–adsorption transition point. Binary and ternary mixtures of adsorption-active and -inactive solvents were used as eluents and silica gel with a pore diameter of 110 Å as adsorbent. It was possible to separate PSs according to molecular mass on “Sorbfil” silica gel plates for a

number of eluent compositions. The adsorption ability of macromolecules in mixed eluents was evaluated indirectly using Snyder's polarity index, P' , for equilibrium eluent compositions.

The dependences of PS intrinsic viscosity on solvent composition for (1) solvent–non-solvent, (2) two solvents, (3) θ -solvent–solvent mixtures were obtained. It was shown that these dependences are usually nonlinear and for cyclohexane–MEK mixture exhibit a maximum. In this case the polystyrene molecules are thermodynamically more compatible with solvent mixtures than with each component separately.

A correlation was found between Snyder's polarity indices for solvent mixtures used in polymer chromatography under both critical and adsorption conditions and the intrinsic viscosity values of PSs in the same mixtures. This study confirms the relationship between the ability of macromolecules to interact with the stationary phase and their characteristics in solution. Therefore, intramolecular interactions are of great importance for the adsorption behavior of macromolecules.

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