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Use of Linear Solvation Energy Relationships for Characterization of Hypercrosslinked Polystyrene Stationary Phases

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Abstract—Linear solvation energy relationships (LSER model) was tested for the characterization of hypercrosslinked polystyrene (HCPS) stationary phases for high-performance liquid chromatography (HPLC). Analysis of LSER coefficients showed that hydrophobic and electrostatic interactions are the major contributors to retention on HCPS. Fluorine atoms in HCPS increase the fractions of both hydrophobic and electrostatic interactions in the retention. The utility of fluorinated HCPS in the separation of di-*n*-phthalate mixtures by reversed-phase liquid chromatography was demonstrated.

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Reversed-phase high-performance liquid chromatography (RP HPLC) is now one of the most widespread chromatographic techniques for the separation and determination of various classes of organic compounds. Development and optimization of processes for separating complex mixtures is a problem whose solution requires much time and effort, as the stationary phases or the eluent composition must be chosen by trial and error. The predictions of retention and the optimization of separation are of paramount importance for contemporary RP-HPLC versions. As known, retention in RP-HPLC is a complex process, which is affected by many physical and chemical parameters of the system, such as temperature, solute molecules, and compositions of the eluent and stationary phases. A universal theory of retention has not yet been advanced; several empirical retention models are used for this purpose, such as linear solvent strength (LSS) model and linear solvation energy relationships (LSER) model. There is also the global LSER model, which accounts for both aforementioned theories; this theory is used to describe retention in complex systems with multicomponent stationary phases [1, 2].

Linear solvent strength model. It was shown in [3, 4] that, in binary aqueous–organic eluents (which are most abundant RP-HPLC eluents), the retention of an analyte can be approximately described by representing the eluent composition as quasi-linear functions of the volume of the organic phase in the eluent ϕ:

$$\log k' = \log k'_w - S\phi. \quad (1)$$

Here, k' is the retention factor of the analyte at a given concentration of the organic solvent in the eluent, k'_w is the sorbate capacity coefficient in the absence of organic solvent (usually determined by extrapolation of the results obtained for binary eluents to zero ϕ), and S is a parameter that controls the elution power for a particular stationary phase. $\log k'_w$ and S are determined by measuring the retention of the compound with the use of two eluents that differ in the concentrations of the organic solvent. This calibrated equation can be used to predict the retention of a compound with different eluent compositions. In transfer from one analyte to another, the equation should be calibrated for each analyte. Linear solvation energy relationships are a more perfect technique.

Linear solvation energy relationships. This concept was developed in [5, 6]. For a great many chemical systems, there are linear relationships between some properties and the free energy of the reaction, the free energy of transition, or the activation energy, parameters related to the fundamental parameters of the solvents and solutions. According to this concept, chromatographic retention is described by a linear relationship between the log retention factor ($\log k'$) and the parameters that describe the free energy of the reaction:

$$\log k' = c + rR_2 + s\pi_2^* + a\Sigma\alpha_2^H + b\Sigma\beta_2^H + vV_x, \quad (2)$$

Here, the subscript "2" indicates that the parameter (descriptor) is a characteristic of the sorbate, the superscript "*H*" indicates that the quantity describe the ability of the sorbate to proton interactions, V_x is the MacGowan characteristic molar volume (100 cm^3/mol), π is the dipole moment and polarizability of the sorbate, α is the ability to donate an electron pair in hydrogen bonding (basicity), β is the ability to accept an electron pair in hydrogen bonding (acidity), and R_2 is the ability of the

sorbate to interact with n and π electrons. The sorption descriptors V_x and R_2 can be easily calculated, whereas the other descriptors are derived experimentally from liquid–liquid partition and gaseous or liquid systems. Each descriptor of the sorbate is multiplied by some factor (an unknown variable), which represents the distinctions between the eluent and stationary phases. The factor r in Eq. (2) characterizes the ability of the sorbent to interact with n and π electrons of the components of the sample; s, the polarity and polarizability; a and b, the ability to accept and donate an electron pair in hydrogen bonding; v, the hydrophobicity of the stationary phase; and c is a constant. These parameters are calculated from experimental data for various sorbates and the set composition of the eluent.

To determine all constants, one should determine the values of six parameters, which can be done by studying retention for at least six sorbates. However, it is advisable to use 25 various sorbates for the determination of each parameter for the set eluent. Only in this case can the LSER model be used to describe the sorbent, predict the retention, and optimize the separation on this sorbent for the set eluent. We should note that the LSER model designed for one eluent cannot be used for another eluent even on the same column [2, 7, 8]. An important strength of the LSER model is its ability to theoretically describe stationary phases and compare them with one another.

Global LSER model. A weakness of the aforementioned methods is their limited applicability. The LSS model applies only to one particular compound. The LSER model applies only to one solvent. Therefore, it was proposed to combine the two models [2]; the combined model was referred to as the global LSER model.

Inasmuch as the parameters $\log k'_w$ and S in the LSS model are, in fact, the free energy parameters for a certain process, they can be adapted to the LSER model. From this, each parameter can be described by the LSER model:

$$\log k'_w = c_w + v_w V_2 + s_w \pi_2^* + a_w \Sigma\alpha_2^H + b_w \Sigma\beta_2^H + r_w R_2, \quad (3)$$

$$S = c_S + v_S V_2 + s_S \pi_2^* + a_S \Sigma\alpha_2^H + b_S \Sigma\beta_2^H + r_S R_2. \quad (4)$$

Substitution of models (3) and (4) for coefficients in the LSS equation gave

$$\log k' = \log k'_w - S\phi = c_w - c_S\phi + v_w V_2 - v_S\phi V_2 + s_w \pi_2^* - s_S\phi\pi_2^* + a_w \Sigma\alpha_2^H - a_S\phi\Sigma\alpha_2^H + b_w \Sigma\beta_2^H - b_S\phi\Sigma\beta_2^H + r_w R_2 - r_S\phi R_2. \quad (5)$$

This, in turn, shows that each coefficient in the LSER equation can be represented as a function of ϕ, i.e., a function of the eluent composition.

Hypercrosslinked styrene stationary phases. Polystyrene–divinylbenzene (PS–DVB) copolymer stationary phases appeared several decades ago [9]; conventionally, they have been used in gas chromatography and in several versions of liquid chromatography, e.g., size-exclusion chromatography. However, RP-HPLC polymer stationary phases satisfying stiffness and monodispersity requirements were manufactured in the late 1970s; their development was slowed by the difficulty of synthesizing monodisperse microparticles with reproducible properties and the required mechanical strength. The following parameters are decisive for RP-HPLC polymer stationary phases: the nature of the monomer, crosslinker, and grafted groups, which controls the hydrophobicity of the sorbent and the retention mechanism on this sorbent; the crosslinker concentration in the polymer or crosslink density, which controls the mechanical strength and stiffness of the sorbent and, therefore, its applicability to HPLC (the polymer stiffness increases with crosslink density); and the pore structure (specific surface area, pore volume, and pore diameter) and the pore size, which influence the efficiency of the stationary phase [10, 11].

Polymer stationary phases have several advantages over chemically modified silica gels (CMSG). First of all, these stationary phases have a higher hydrolytic stability; therefore, they can be used over a wide pH range (for most stationary phases, from 1 to 13). They have a uniform surface: their structure is free of adsorption sites like silanol groups in CMSG. Therefore, the use of polymer stationary phases avoids problems encountered in using CMSG for the separation of molecules bearing basic groups, such as irreversible adsorption and peak broadening. The weaknesses of polymer stationary phases are due to the structure of the polymer matrix. First, the sorbent volume depends on the eluent composition: unlike CMSG, polymer stationary phases swell noticeably in organic and aqueous–organic solvents. Second, columns packed with a polymer stationary phase are inferior to CMSG in their efficiency: the number of theoretic plates (TP/m) for polymer stationary phases with average particle sizes of than 5 μm does not exceed 50–60 thousands, whereas for silica gel stationary phases with the same particle sizes, the number of theoretical plates can reach 80 thousands. In addition, the efficiency of polymer stationary phases is strongly affected by temperature, the nature and concentration of the organic solvent in the eluent, the retention time, and the types of molecules to be separated.

In the late 1960s, an original process was proposed for the synthesis of polystyrene stationary phases as distinct from the synthesis of other PS–DVB stationary phases. The underlying idea of this process is the extra crosslinking of styrene + 0.7% divinylbenzene copolymer, ultimately swollen in dichloroethane, by monochlorodimethyl ether in the presence of a Lewis catalyst ($AlCl_3$, $FeCl_3$, or $SnCl_4$) [12–15]. The polymer prepared in this way is fundamentally different from the

Table 1. Characteristics of the stationary phases used

Name	Stationary phase	S_{sp}, m^2/g	d_r, μm	d_{pore}, Å
HNM KM1/021	Hypercrosslinked polystyrene	1000	3	1500
PLRP-S	Polystyrene	414	5	100
MN KS/R508	Hypercrosslinked polystyrene	–	5	–
MN KS/R505	Hypercrosslinked polystyrene Direct MN	–	10	–
Fluorinated MN KS/R505	XeF_2-fluorinated hypercrosslinked polystyrene Direct NM	–	10	–

structure of PS–DVB stationary phases. In this case, virtually all benzene rings of the starting polystyrene backbone are additionally linked to each other via stiff methylene bridges, and the degree of crosslinking of the resulting stationary phase is more than 100%. Hypercrosslinked polystyrene stationary phases are neutral hydrophobic polymers whose surface can be modified by various groups. Their pore structure can be regulated during the synthesis: HCPS can have either mono- or bimodal pore-size distribution; pore sizes range from micropores with d_{pore} of about 10 Å to macropores with d_{pore} of about 1000 Å [16–18]. These stationary phases have high specific surfaces (more than 1000 m^2/g) and rather large pore volumes (up to 1.1 cm^3/g); they ensure quantitative extraction of many organic and inorganic compounds from large volumes of aqueous solutions [19, 20]. Hypercrosslinked polystyrene stationary phases have high thermostability and are used in gas chromatography. They are compatible with any organic solvent and are not altered over the entire ranges of the pHs and ionic strengths of the eluents used. Hypercrosslinked polystyrene stationary phases are characterized by very low spatial densities of polymer chain packing, with the mechanical strength being conserved; therefore, most part of the highly developed surface of this material is accessible to sorbate molecules [14, 21].

This work studies the chromatographic properties of HCPS stationary phases and a fluorinated modification using the LSER model and compares them with lightly crosslinked analogues.

EXPERIMENTAL

Equipment. The chromatographic system used comprised eluent tank, Beckman 114M high-pressure pump, Rheodyne 7125 injector with a 20 μL loop, Carlo Erba Instrument Micro-UVIS 20 spectrophotometric detector, steel column (75 × 2 mm), and Ampersand MultiChrome data processing system. Samples were aspirated with a 25 μL Hamilton microsyringe.

Reagents and solutions. The stationary phases used were as follows: HCPS stationary phases HNM KM1/021, MN KS R508, MN KS R505, and XeF_2-fluorinated MN KS R505; and PS–DVB phase PLRP. The parameters of these stationary phases are listed in Table 1.

The HPLC eluents used were water + acetonitrile mixtures of various compositions prepared from chromatographically pure acetonitrile (Reakhim) and distilled water. The following compounds were used to study the chromatographic properties: phenol, *o*-cresol, *p*-cresol, *p*-aminophenol, *p*-chlorophenol, *p*-iodophenol, *o*-chlorophenol, 2,3-dichlorophenol, 2,4,6-trichlorophenol, 3-chloro-4-methylphenol, pentachlorophenol, *p*-methoxyphenol, 3,4-dimethylphenol, *o*-nitrophenol, *m*-nitrophenol, *p*-nitrophenol, *p*-cyanophenol, toluene, ethylbenzene, *p*-diethylbenzene, *n*-propylbenzene, *n*-butylbenzene, *n*-pentylbenzene, *n*-nonylbenzene, dimethyl phthalate, diethyl phthalate, di-*n*-propyl phthalate, di-*n*-butyl phthalate, di-*n*-pentyl phthalate, di-*n*-hexyl phthalate, benzene, naphthalene, anthracene, fluorene, *p*-terphenyl, chrysene, bromobenzene, *o*-dichlorobenzene, benzyl alcohol, benzaldehyde, acetophenone, benzophenone, methoxybenzene, benzonitrile, *p*-nitrotoluene, nitrobenzene, divinylbenzene, resorcinol, pyrogallol, β-naphthol, and pyridine (all reagents were at least of pure for analysis grade). Standard solutions of all chemicals were prepared in methanol (1 mg/mL).

RESULTS AND DISCUSSION

Comparative characterization of stationary phases by the LSER model. The LSER model, which is the optimum existing model, was proposed to describe the retention on stationary phases. The retention of 18–30 model compounds (Table 2) was studied on each stationary phase. The eluent used was 60 vol % acetonitrile plus 40 vol % water.

Retention factors were determined, and the coefficients of the LSER equation were calculated by linear regression using SPSS 12.0.1 for Windows (Table 3).

The positive values of v for all stationary phases considered indicate their hydrophobicity; the HCPS stationary phases MN KS/R505 and MN KS/R508 have the highest hydrophobicity, because the carbon fraction in them is very high relative to the other elements. In its hydrophobicity, this HCPS approaches graphite (both stationary phases have a compact framework built of crosslinked aromatic rings); therefore, hydrophobic interactions are the main contributors to the retention on polystyrene stationary phases. Positive r values indicate that π–π and π–n electron interactions make a cer-

Table 2. Descriptors of model compounds; stationary phase: $CH_3CN–H_2O$ (60 : 40) [6, 8, 23]

Model compound	R_2	π_2^*	$\Sigma\alpha_2^H$	$\Sigma\beta_2^H$	V_x
Benzene	0.610	0.52	0	0.14	0.7164
Toluene	0.601	0.52	0	0.14	0.8573
Ethylbenzene	0.613	0.51	0	0.15	0.9982
Bromobenzene	0.882	0.73	0	0.09	0.8914
Naphthalene	1.340	0.92	0	0.20	1.0854
Anthracene	2.290	1.34	0	0.26	1.4540
Fluorene	1.588	1.03	0	0.20	1.3565
Benzaldehyde	0.818	1.00	0	0.39	0.8730
p-Nitrotoluene	0.870	1.11	0	0.38	1.0315
Benzyl alcohol	0.803	0.87	0.33	0.56	0.9160
Acetophenone	0.818	1.01	0	0.48	1.0139
Benzophenone	1.447	1.50	0	0.50	1.4808
o-Dichlorobenzene	0.872	0.78	0	0.04	0.9612
Nitrobenzene	0.871	1.11	0	0.28	0.8906
Benzonitrile	0.742	1.11	0	0.33	0.8711
β-Naphthol	1.520	1.08	0.61	0.40	1.1440
Dimethyl phthalate	0.780	1.41	0	0.88	1.4288
Resorcinol	0.980	1.00	1.10	0.58	0.8340
o-Cresol	0.840	0.86	0.52	0.30	0.9160
p-Cresol	0.820	0.87	0.57	0.32	0.9160
2,4,6-Trichlorophenol	1.010	1.24	0.820	0.08	1.1420
2,4-Dinitrophenol	1.200	1.50	0.10	0.55	1.1240
2-Chlorophenol	0.853	0.88	0.32	0.31	0.8975
Divinylbenzene	1.280	0.50	0	0.15	0.6000
Phenol	0.805	0.89	0.60	0.31	0.7751
p-Cyanophenol	0.940	1.63	0.79	0.29	1.0389
Pentachlorophenol	1.220	0.87	0.96	0.01	1.3871
3-Methyl-4-chlorophenol	0.920	1.02	0.65	0.23	1.0382
p-Chlorophenol	0.915	1.08	0.67	0.20	0.9152
p-Iodophenol	1.380	1.22	0.68	0.20	0.9218
o-Nitrophenol	1.015	1.05	0.05	0.37	0.9253
m-Nitrophenol	1.050	1.57	0.79	0.23	1.0266
p-Nitrophenol	1.070	1.72	0.82	0.26	1.0303
n-Propylbenzene	0.604	0.50	0.00	0.15	1.1390
n-Butylbenzene	0.600	0.51	0.00	0.15	1.2800
p-Methoxyphenol	0.900	1.17	0.57	0.48	0.9750
Pyridine	0.631	0.84	0.00	0.52	0.6753

tain contribution to the sorbent–sorbate interactions. Negative values indicate the nonexistence of such interactions, which can be because of the structure of the stationary phases. The factor *s*, which describes the polarity and polarizability, is positive only for MN KS/R505. This means that this stationary phase will retain polar compounds; the other stationary phases are less prone to this. At the same time, we trace a rise in *s* in response to increasing crosslink density. We also show that each of the aforementioned sorbents, to some degree, has both acid and base properties.

Electrostatic interactions, along with hydrophobic ones, can contribute significantly to the retention of sorbates on HCPS. Not only does the existence of fluorine

Table 3. Coefficients in the LSER equations for the stationary phases studied; eluent: $CH_3CN–H_2O$ (60 : 40)

Stationary phase	LSER coefficients					
	c	*r*	*s*	*a*	*b*	*v*
KS/R 505	−0.80 ± 0.39	−0.42 ± 0.18	0.44 ± 0.49	1.08 ± 0.68	−1.79 ± 0.50	1.53 ± 0.33
KS/R 508	−0.13 ± 0.63	1.65 ± 1.22	−0.79 ± 0.58	−0.58 ± 0.33	−0.84 ± 0.51	1.44 ± 0.50
PLRP–S	0.52 ± 0.29	1.15 ± 0.22	−0.39 ± 0.18	−0.21 ± 0.13	−1.73 ± 0.30	0.70 ± 0.28
HNM	−0.43 ± 0.21	0.86 ± 0.17	−0.28 ± 0.11	−0.59 ± 0.10	−1.89 ± 0.22	0.90 ± 0.23
SiO_2-ferrocene [24]	−0.72 ± 0.06	0.40 ± 0.03	0.12 ± 0.04	−0.55 ± 0.07	–2.31 ± 0.09	0.70 ± 0.08

Table 4. Coefficients in the LSER equations for unmodified and fluorinated HCPS; eluent: $CH_3CN–H_2O$ (60 : 40)

Stationary phase	LSER coefficients					
	c	*r*	*s*	*a*	*b*	*v*
KS/R 505	−0.81 ± 0.39	−0.42 ± 0.18	0.44 ± 0.49	1.08 ± 0.68	−1.79 ± 0.50	1.53 ± 0.33
Fluor KS/R 505	−0.26 ± 0.08	0.30 ± 0.07	−0.16 ± 0.09	0.53 ± 0.11	−1.09 ± 0.13	1.17 ± 0.12

atoms in modified HCPS change the strength of electrostatic interactions, but it also influences the hydrophobicity of the stationary phase and the π-electron-density distribution compared to that in unmodified HCPS.

To determine the parameters of stationary phases by the LSER model, we studied the retention of model compounds (Table 2) with various sets of descriptors on fluorinated MN KS/R505 and unmodified NM KS/R505. The fact that only two factors (v and r) in Eq. (2) are positive (Table 4) means that the retention under the specified conditions is mainly due to π–π and hydrophobic interactions. These results correlate with earlier data, which make it clear that hydrophobic interactions for unmodified HCPS are stronger. The high polarity is manifested for the fluorinated stationary phase: fluorine is not only an inductive acceptor but also a mesomeric donor that redistributes the electron density in benzene rings of the polymer matrix of the stationary phase.

In order to ascertain the retention mechanism on HCPS, we compared our data with the LSER retention data obtained on ferrocene-modified silica gel [24]. In choosing this reference stationary phase, we were guided by the following: HCPS can retain metals, and the retention mechanism resembles that of iron retention in the structure of ferrocene; the surface structure formed by grafted ferrocene molecules on the stationary phase (many close-lying aromatic rings) is similar to the HCPS structure. Comparison with the data obtained for HCPS stationary phases shows that ferrocene-modified silica gel has a hydrophobic surface (v in Eq. (2) is positive), and approaches the polystyrene stationary phase PLRP in the contribution of hydrophobic interactions. This is due to the occurrence of aromatic rings on the surface of modified silica gel; these rings are capable of electron-density redistribution. A positive value of r indicates that π–π and π–n electron interactions contribute to the sorbent–sorbate interactions. For the polystyrene and HCPS stationary phases, s increases with increasing crosslink density (i.e., the polarity and polarizability of the sorbent increase because of a rise in the electron density, which is due to increasing spatial density of benzene rings). For ferrocene-modified silica gel, the positive s value is due to the fact that ferrocene molecules themselves are rather highly polarizable. We also show that, because of iron atoms contained in its molecules, ferrocene-modified silica gel has higher basic properties than polymer sorbents.

In this work, we attempted to describe and compare the hydrophobicities of fluorinated HCPS under various conditions. For this purpose, we calculated $\alpha(n_c)$ which is the retention increment or an increase in the retention induced by addition of one methylene group to the structure of a model compound; e.g., for the retention of several alkylbenzenes, the following equation was used:

$$\log k' = \text{const} + \alpha(CH_2)n_c. \quad (6)$$

Here, $\alpha(CH_2)$, which is the $\log k'–C_n$ slope, can be considered as a measure of the alkyl selectivity or affinity of the sorbent. Calculations show that fluorinated HCPS acquires the highest $\alpha(CH_2)$ values with decreasing acetonitrile concentration in the eluent (Fig. 1). Compounds such as *n*-alkylbenzenes and di-*n*-alkyl phthalates are convenient model compounds; their retentions are frequently used to compare the selectivities of RP-HPLC stationary phases. Figures 2 and 3 display chromatograms for mixtures of *n*-alkylbenzenes and di-*n*-alkyl phthalates obtained on fluorinated HCPS.

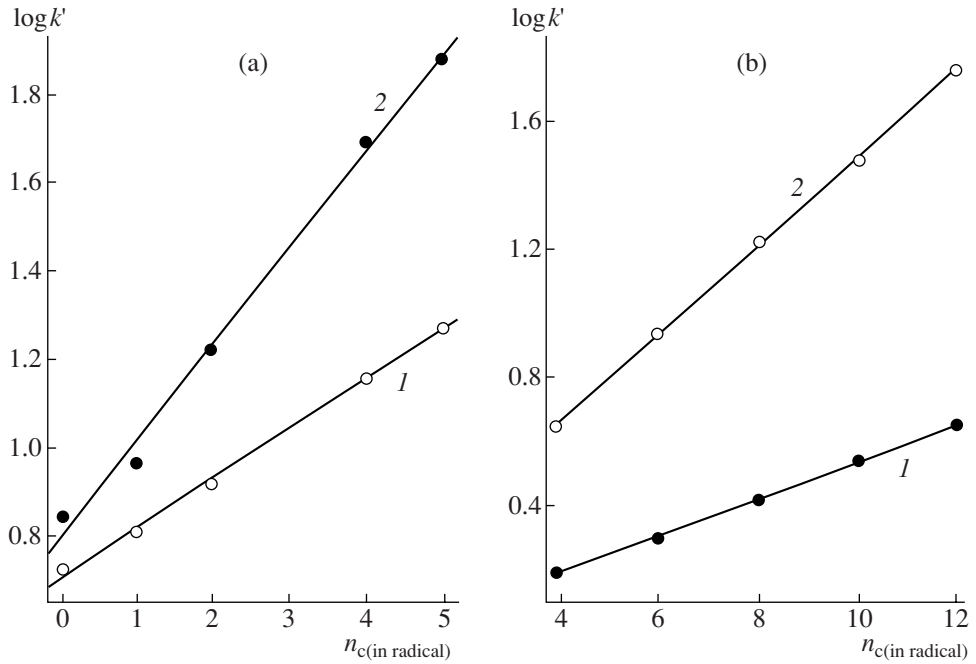

Fig. 1. Retention of (a) alkylbenzenes and (b) dialkylphthalates vs. number of carbon atoms in the pendant chain for elution with $CH_3CN–H_2O$ mixtures: (*1*) 70 : 30 and (*2*) 60 : 40.

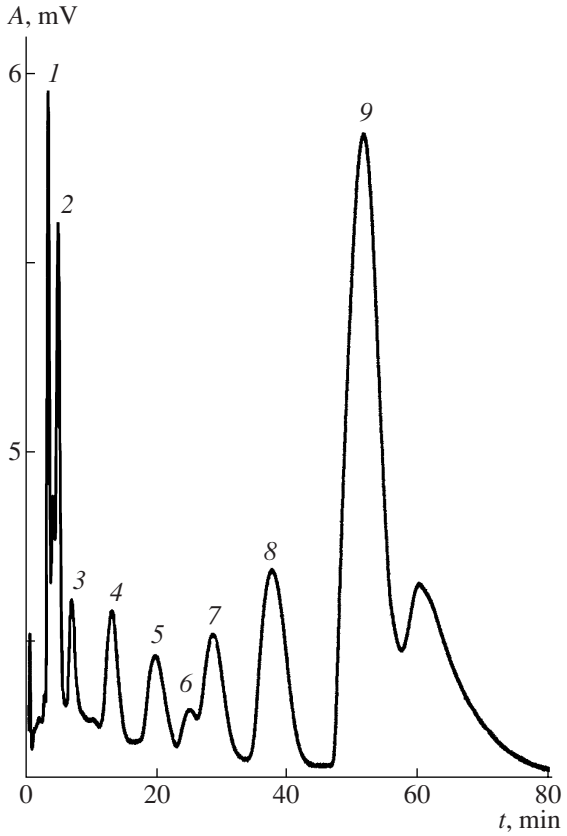

Fig. 2. Chromatogram of an *n*-alkylbenzene mixture (column, fluorinated HCPS, 75 × 2 mm; eluent, $CH_3CN–H_2O$, 70 : 30; flow rate, 0.2 mL/min): (*1*) benzene, (*2*) toluene, (*3*) ethylbenzene, (*4*) *n*-propylbenzene, (*5*) *n*-butylbenzene, (*6*) *n*-pentylbenzene, (*7*) *n*-hexylbenzene, (*8*) *n*-octylbenzene, and (*9*) *n*-nonylbenzene.

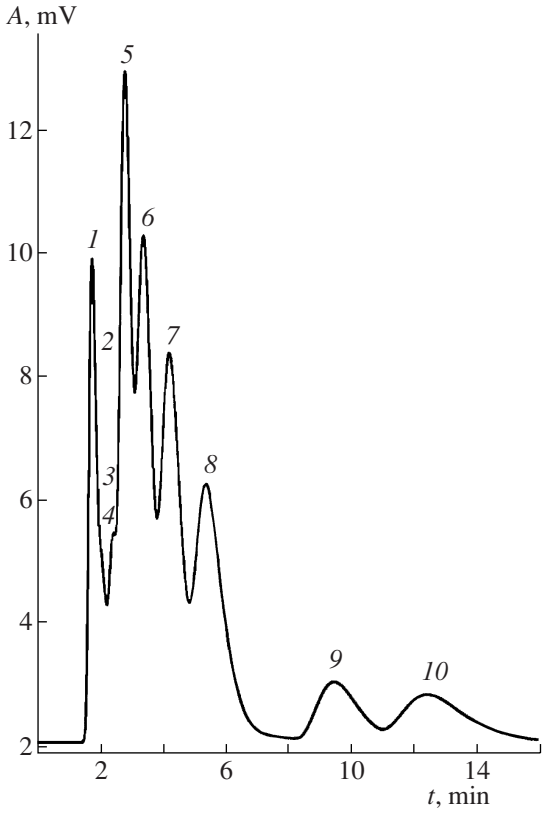

Fig. 3. Chromatogram of a di-*n*-alkyl phthalate mixture (for the chromatography parameters, see Fig. 2): (*1*) dimethyl phthalate, (*2*) diethyl phthalate, (*3*) di-*n*-propyl phthalate, (*4*) di-*n*-butyl phthalate, (*5*) di-*n*-pentyl phthalate, (*6*) di-*n*-hexyl phthalate, (*7*) di-*n*-heptyl phthalate, (*8*) di-*n*-octyl phthalate, (*9*) di-*n*-decyl phthalate, and (*10*) di-*n*-undecyl phthalate.

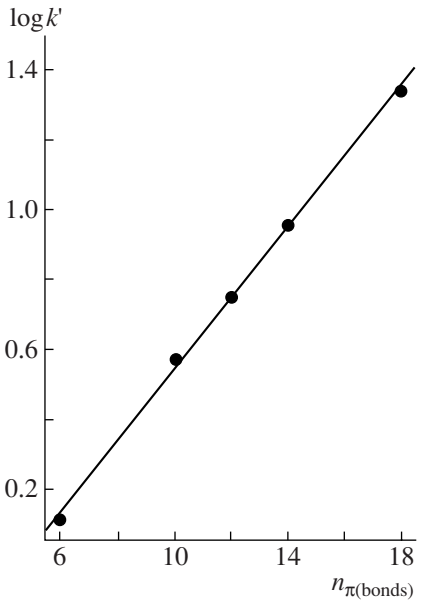

Fig. 4. Retention of alkylbenzenes vs. number of aromatic carbon atoms (π bonds) in their molecule.

The study of HCPS in [22] showed that this type of stationary phase has a high affinity to phenyl, which indicates a considerable contribution of π–π interactions into the retention mechanism on this stationary phase. An analogue of the above-described method can be used if aromatic compounds are used as standards for the characterization of stationary phases.

In this case, the relationship becomes

$$\log k' = \text{const} + \alpha_\pi n_\pi. \quad (7)$$

Here, α_π is the characteristic of the relative strength of π–π interactions between sorbates and various sorbents. In order to estimate the strength of π–π interactions on the fluorinated HCPS stationary phase, we obtained k' values for several polyaromatic compounds containing one to five fused rings. We chose sorbates with near-planar molecular geometry and, thus, with the minimal role of the structural selectivity or steric recognition. Provided that this condition is fulfilled, $\log k'$ is a near-linear function of the number of π electrons in a sorbate molecule (n_π) (Fig. 4). The strong retention of aromatic compounds on HCPS and the considerable contribution of π–π interactions into the retention mechanism are explained as follows. First, hypercrosslinked macronet polymers have very low spatial densities of chain packing. Therefore, most part of the highly developed internal surface of this material is accessible to sorbate molecules; i.e., sorbate–sorbent contact here can be more intimate than for other stationary phases. Second, conjugated or even fused aromatic systems can form during the crosslinking of polystyrene chains by methylene groups, in addition to diphenylmethane-type structures. The color of HCPS stationary phases provides indirect evidence in favor of this scenario.

The above-described approaches can be used both for predicting the retention of model compounds in a homologous row and for comparing and describing stationary phases.

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