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SYNTHESIS AND INVESTIGATION OF POROUS PYROCARBON-MODIFIED SILICAS

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SUMMARY

Porous silica-based pyrocarbon adsorbents were studied using adsorption, gas and liquid chromatography. A more uniform deposition of pyrolysis products on the surface was observed at low benzene conversion rates, at pyrolysis temperatures below 850°C and when a more heat-resistant macroporous silica with pore diameter, $d > 300$ Å was used as the support. Gas chromatography and adsorption studies have shown that silica modified with pyrocarbon has similar chromatographic properties to acetylene and thermal carbon blacks, but is less homogeneous both geometrically and chemically. The high affinity of carbosilica gel for polyaromatic hydrocarbons and its high sensitivity to the geometric (steric) structure of such molecules in liquid chromatography are described.

INTRODUCTION

In spite of some unique properties, the utilization of graphitized thermal carbon blacks (GTCBs), well known carbon adsorbents, is practically confined to gas adsorption chromatography. GTCBs are not popular in liquid chromatography because their mechanical strength is inadequate and it is difficult to produce small (5–10 μm) granules. Attempts to produce a carbon-surface adsorbent devoid of these defects and preserving all the advantages of GTCB (high dispersion interaction energy, chemical homogeneity and high selectivity with respect to geometric isomers) and suitable for use in high-performance liquid chromatography (HPLC) resulted in the production of so-called pyrocarbon adsorbents. These are produced by applying thin layers of pyrocarbon (generally using heterogeneously catalyzed benzene pyrolysis[1]) to the surface of a carrier: carbon black[2–4] or various silicas[5–8]. Kiselev, Guiochon and other workers have described, among other things, the utilization of porous silica-based pyrocarbon adsorbents in liquid chromatography. When polar eluents are used, these adsorbents are highly selective with respect to homologues and geometric isomers. Pyrocarbon-modified industrial silicas have been used as inert carriers of liquid phases for gas chromatography (GC)[9]. A GC investigation of the properties of pyrocarbon adsorbents produced by pyrolysis of alcohols is described by Leboda[10].

Although they show promise, these adsorbents and carriers have not won great

recognition in chromatography. This is largely due to problems of producing adsorbents with chemically "perfect" and geometrically homogeneous surfaces. As a result, the chromatographic peaks are asymmetric. The rather low efficiency of pyrocarbon adsorbent columns used for HPLC calls for the development of methods for packing these columns with optimally sized particles. The high dispersion interaction energy of the pyrocarbon surface results in prolonged retention and considerable broadening of peaks of strongly retained compounds[2-4]. Thus, it is necessary to carry out an extensive study of the problems pertaining to the production of pyrocarbon adsorbents that meet the requirements of various fields of chromatography. The aim of this work is to optimize the conditions for synthesis of these adsorbents in order to improve the structural, adsorption and chromatographic properties of the pyrocarbon surface, and to study the relationship between these properties and the quantity and type of pyrolysis product deposited. Porous silica-based pyrocarbon adsorbents have been studied using adsorption, gas and liquid chromatography.

EXPERIMENTAL

Procedures described by Bebris *et al.*[1] were used for the synthesis of pyrocarbon adsorbents, *i.e.* carbosilica gels and carbosilochroms. The modification was carried out in a vertical quartz reactor heated by an electric furnace and having an inner porous quartz partition on which a layer of ground quartz ($\approx$ 1-mm particles) was placed, followed by the adsorbent. Pyrolysis was carried out in a flow-through system at atmospheric pressure in the temperature range 700–900°C. The carrier gas, *i.e.*, helium, saturated with benzene vapours was fed at the reactor bottom at a pre-set rate (75–100 ml/min) so as to form a mobile layer in the reaction zone. After pyrolysis, the supply of benzene and the heating were discontinued, the reactor was allowed to cool to room temperature in a flow of helium and the adsorbent was separated from quartz with the help of sieves. The quantity of carbon on the adsorbent surface was determined by the weight method by combustion in the air at 550°C. To study the effect of the synthesis conditions on the nature of the coatings produced, the pore structure and the GC properties of pyrocarbon adsorbents, commercial samples of macroporous silica gels MCA and LiChrospher Si-500 as well as Silochrom C-120 were used as the initial adsorbents. The specific surface areas, S_{Kr}, of initial and modified prototype samples were estimated from low-temperature isotherms for krypton vapour adsorption.

The surface concentration of pyrocarbon, α_c, was calculated from data on the quantitation of the pyrolysis products and the values of S_{Kr} for the adsorbents following annealing of the carbon deposits. The pore volume, "v", was defined as that of liquid benzene adsorbed at the saturated vapour pressure. The average pore diameter was calculated using the formula $\bar{d} = 4v/S_{Kr}$. Structural characteristics of the silochrom and carbosilochrom (specific surface area, $S_{C_6H_6}$; specific surface area of the adsorption film formed by the time capillary-condensation hysteresis begins, S; pore diameters, $\bar{d}$ and effective Kelvin pore diameter, d_k) were also evaluated from complete adsorption–desorption isotherms for benzene vapour on these samples at 25°C. These data were used to plot pore-volume distribution curves as a function of the effective Kelvin pore diameters.

Whereas the S values of pyrocarbon adsorbents with $\alpha_c \geqslant 3$ mg/m² were

estimated, values of ω_m (area occupied by a molecule in the dense monolayer) for krypton and benzene were taken as 16.3[11] and 40 Å² (ref. 12), as was the case with GTCB. As regards other samples, the corresponding values were 21.5[13] and 49 Å² (ref. 14), respectively.

Measurements of the adsorption isotherms of benzene, hexane and water were done using an adsorption–vacuum installation equipped with McBain scales[15] at 25°C, p/p_0 ranging from 0 to 0.35.

Gas chromatography was performed on a Tsvet-4″ chromatograph with a flame ionization detector. The sizes of the adsorbent grains were 0.25–0.5 mm. Nitrogen was used as the carrier gas with steel columns (100 × 0.4 cm).

Liquid chromatography was performed using pyrocarbon adsorbents produced from microspherical macroporous silica gel LiChrospher Si-500 (Merck) with particles of about 10 μm. The Varian 5060, with a spectrophotometric detector, and Spectra Physics liquid chromatographs, with an UV detector (λ = 254 nm), were used. Hexane, heptane and their mixtures with chloroform, as well as methanol–water served as the eluents. The time required for carbon tetrachloride (when eluted by hexane, heptane and their mixtures with chloroform) and gallic acid (elution with methanol) to emerge from the column is taken as the zero time.

RESULTS AND DISCUSSION

A. Effect of pyrolysis conditions on the properties of modified adsorbents

According to Rudenko[16], pyrolysis gives rise to multistage dehydrocondensation of benzene molecules. Thus, high-molecular-weight polycyclic compounds (carboids) are formed. They differ in the extent of condensation, have an aromatic nature and are treated as fragments of graphite structure. When carboids adhere to one another to form batches, graphite microcrystals are formed in random orientations with respect to the surface.

The effect of the pyrolysis conditions on the quantity of carbon products on the silica gel surface is summarized in Table I. As expected, higher pyrolysis temperatures are conducive to the accumulation of surface carbon. Thus, if the duration of the experiment and benzene feed rate are constant, an increase in the temperature from 800 to 900°C causes the concentration of carbon products to increase five-fold. At constant pyrolysis temperature, higher yields of surface carbon are observed after long treatments and at greater benzene feed rates. The benzene feed rate at 850–900°C was experimentally found not to exceed 3 g/h; greater rates of conversion of high concentrations of hydrocarbon result in the formation of loose disperse carbon black.

From Table I it follows that the rate of accumulation of carbon products is greater in the first hour of pyrolysis than in the second one. Some authors[17] are of the opinion that the pyrocarbon film is less catalytically active than when further away from the initial silica surface. The inhibition of the pyrolysis product accumulation process in our experiments seems also to be caused by partial reduction in the contact surface. Indeed, from the data of Table I it follows that the S and v values are decreased upon benzene pyrolysis, particularly at 900°C.

Comparison of the v values of the initial silica gel carbon-modified samples and similar samples after burning out the pyrolysis products (Table I) shows that

TABLE I

EFFECT OF BENZENE PYROLYSIS CONDITIONS OR THE QUANTITY OF CARBON PRODUCTS ON THE SURFACE OF MACROPOROUS SILICA GEL AND ON THE STRUCTURAL CHARACTERISTICS

Sample	Pyrolysis temperature (°C)	Time (h)	Benzene feed rate (g/h)	Pyrocarbon concn. (%, w/w)	α_c (mg/m²)	Before annealing			After annealing		
						S_{Kr} (m²/g SiO₂)	V (cm³/g SiO₂)	$\bar{d}$ (Å)	S_{Kr} (m²/g)	V (cm³/g)	$\bar{d}$ (Å)
Initial	–	–	–	–	–	–	–	–	40	0.69	690
1	800	1	3	4.5	1.1	–	0.66	–	40	0.69	690
2	850	1	3	16.3	4.0	38	0.57	600	41	0.64	670
3	850	2	3	26.8	6.9	–	–	–	–	–	–
4	900	1	3	22.0	5.6	33	0.41	500	38	0.53	620
5	900	2	3	22.8	7.6	31	0.37	480	30	0.47	630
6	900	2	1.5	14.0	4.7	–	–	–	–	–	–

TABLE II

STRUCTURAL CHARACTERISTICS OF ADSORBENTS

Adsorbent and processing conditions	Specific surface area (m^2/g SiO_2)			V, (cm^3/g SiO_2)	d_K ($\AA$)	$\bar{d}$ ($\AA$)
	S_{Kr}	$S_{C_6H_6}$	S			
Silochrom C-120 (initial)	145	140	150	1.20	290	330
Carbosilochrom, pyrolysis (850°C, 1 h), $\alpha_c = 1.3$ mg/m^2	120	125	140	1.03	290	310
Carbosilochrom after burning out	145	140	150	1.20	290	330

changes in the pore structure in modified adsorbents are caused by two processes: caking of the silica support itself and deposition of carbon products on the surface of silica particles. Thus, after pyrolysis of benzene at 900°C for 1 h, the volume of the silica gel pores is reduced by 23% as a result of silica caking (from 0.69 to 0.53 cm^3/g) and by another 18% (to 0.41 cm^3/g) following deposition of carbon products. Both processes result in a decrease in the $\bar{d}$ value. Somewhat different changes in the pore structure were observed by us when silica gel Spherisorb S200-W (S = 215 m^2/g) was modified with pyrocarbon[6]. During benzene pyrolysis, at 750°C, the value of S decreased more than two-fold and the pores expanded. Such changes in S and $\bar{d}$ are common upon caking of silicas containing admixtures of alkali metals[18]. The benzene pyrolysis reaction carried out on Silochrom C-120, a more heat-resistant, high-purity silica adsorbent, helped to eliminate changes in the structural characteristics caused by support caking. From the data given in Table II it follows that deposition of carbon is the only factor responsible for the lower values of S and v upon modification of Silochrom C-120; when the pyrolysis products were burnt out the structural characteristics of the samples were restored completely.

Determination of the apparent density of carbon products, δ, helped to evaluate the character of their deposition on the adsorbent surfaces. The values of δ were calculated from the formula $\delta = (m_1 - m_2)/(v_2 - v_1)$, where m_1 is the weight of a portion of the modified sample, v_1 is the volume of pores in this portion, v_2 and m_2 are the volume of pores and weight of sample after burning out of the pyrolysis products. For carbon coatings obtained on silica gel MCA at 850 and 900°C and on Silochrom at 850°C after 1 h, the δ values are 1.8, 1.5 and 1.4 g/cm^3, respectively, i.e., less than the density of graphite itself (≈ 2.2 g/cm^3). These data indicate a non-uniform deposition of the modifying layers on the adsorbent surface. It appears that when pyrolysis takes place and carbon surface layers are formed, the mouths of the pores in the adsorbent are narrowed and subsequently close completely. As a result, the entry of benzene into the pore and subsequent deposition on its surface becomes impossible. The higher the pyrolysis temperature and the benzene conversion rate and the narrower the adsorbent pores, the more rapid is the above process. Furthermore, the density of the pyrocarbon deposits on the surface of very large pores can vary depending on the rate of their formation. Earlier we showed[6] that on Sil-
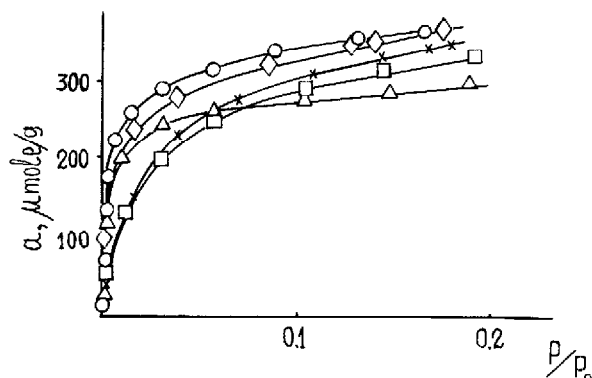
Fig. 1. Isotherms for krypton adsorption on the initial silica gel ($\times$), carbosilica gels modified at 800°C ($\diamond$), 850°C ($\bigcirc$) and 900°C ($\triangle$) and on the sample following annealing of pyrolytic products formed at 900°C ($\square$).

ochrom C-120 containing 20% of pyrolytic products ($\alpha_c = 1.3$ mg/m^2), modification has no effect on the position of the maximum in the curve of pore volume distribution *vs.* their apparent diameters. However, the shape of the distribution curve becomes less symmetrical due to the greater volumes of pores with $d_K < 200$ Å.

The modification of silica adsorbents with benzene pyrolysis products alters the chemical composition of the surface and its adsorption properties. Isotherms for krypton adsorption on samples of modified silica gel are more convex; the region corresponding to a dense monolayer shifts towards smaller relative pressures (Fig. 1). On passing from the initial silica gel to modified samples with $\alpha_c = 1.1$, 4.0 and 5.6 mg/m^2, the constant C of the BET equation related to the pure heat of adsorption increases from 80 to 180, 240 and 380, respectively. This alteration in adsorption properties results in an increase in the dispersion interaction energy of krypton molecules with the graphitized surface of the pyrolytic layer: the greater the percentage of pyrolysis products, the stronger is this interaction.

TABLE III

RETENTION VOLUMES OF SOME SUBSTANCES RELATIVE TO HEXANE ON CARBOSILICA GEL SAMPLES AT 250°C

Sample	Pyroly-sis tem-perature (°C)	α_c (mg/m^2)	$V_{rel.}$						
			Hep-tane	Octa-ne	Ben-zene	Tolu-ene	p-Xy-lene	Diethyl ether	Ace-tone
1	Initial silica gel	—	1.4	1.7	3.0	5.5	9.0	15	83
2	850	1.1	2.4	5.5	1.2	3.0	7.0	2.6	6.6
3	850	4.0	2.3	5.9	1.0	3.0	—	1.1	2.7
4	850	6.9	2.4	5.4	0.9	2.3	6.7	0.5	0.8
5	900	4.7	2.3	5.4	1.0	2.6	6.9	1.1	3.2
6	900	5.6	2.3	5.4	0.9	2.6	7.0	0.8	2.2
7	900	7.6	2.4	5.6	0.8	2.3	7.1	0.5	0.7

TABLE IV

RETENTION VOLUMES OF SOME SUBSTANCES RELATIVE TO HEPTANE ON VARIOUS ADSORBENTS AT 200°C

Adsorbate	$V_{rel.}$			
	Silica gel	Carbosilica gel	Acetylene black	GTCB[19]
Octane	1.4	2.4	2.7	2.9
Nonane	2.4	6.2	7.5	7.7
Decane	3.9	14.9	—	18.2
Benzene	2.6	0.5	0.3	0.3
Toluene	6.2	1.5	1.0	0.9
p-Xylene	13.6	4.1	3.6	3.6
Diethyl ether	27	0.8	0.10	—
Acetone	100	0.3	0.06	—

A similar increase in dispersion interaction energies on carbosilicas is observed for n-alkanes. This is corroborated by the large GC retention volumes, $V_{rel.}$, of heptane and octane volumes relative to that of hexane. From Table III it follows that the application of benzene pyrolysis products to the silica gel causes the $V_{rel.}$ of n-alkanes to increase and that of aromatic hydrocarbons, diethyl ether and acetone to decrease. Compared with the initial silica gel, $V_{rel.}$ of benzene is 2.5 times smaller on the sample with $\alpha_c = 1.1$ mg/m²; in the case of acetone, it is 12.5 times smaller. The smallest values of $V_{rel.}$ for polar molecules were obtained on samples with the maximum concentration of carbon products.

Comparison of the $V_{rel.}$ values on the initial silica gel, carbosilica gel with $\alpha_c = 6.9$ mg/m², acetylene and graphitized thermal blacks (Table IV) shows that the adsorption properties of carbosilica gel approach those of the carbon blacks, but its surface is chemically heterogeneous. This is seen from the $V_{rel.}$ values of benzene, diethyl ether and acetone which are higher on carbosilica gel than on the graphitized thermal and acetylene blacks. The chemical heterogeneity of pyrocarbon samples can be attributed to both the inadequately uniform distribution of pyrocarbon along the silica gel surface and to the presence of oxidized regions on the surface of the pyrocarbon itself. Moreover, silicon carbide is likely to be formed on the silica gel surface during pyrolysis. This fact may have a negative effect on the GC of polar compounds.

The results obtained enable us to describe the carbon deposits on the surface of macroporous silicas formed during benzene pyrolysis at 750–900°C as inadequately dense layers of graphite microcrystals whose depth and homogeneity of distribution on the support surface depend on the conditions of the pyrolysis reaction. A more uniform deposition of pyrolytic products on the surface was observed at low benzene conversion rates and while using macroporous adsorbents. The alteration in the adsorbent structure during the process of benzene pyrolysis is a result of both the heterogeneous carbon deposition and the caking of the adsorbent itself. To reduce these effects it is advisable that pyrolysis be performed at temperatures below 850°C and macroporous silicon adsorbents with $d_K > 300$ Å be used as substrate. While the adsorbents are being modified the specific adsorption centres of silica are blocked;

TABLE V

EFFECT OF BENZENE PYROLYSIS CONDITIONS ON THE QUANTITY OF PYROCARBON
DEPOSITED ON THE SURFACE OF SILICA GEL LICHROSPHER Si-500 ($S = 38 \text{ m}^2/\text{g}$)

Sample	Pyrolysis tempera- ture (°C)	Pyroly- sis time (h)	Benzene feed rate (g/h)	Quantity of carbon pro- ducts (%, w/w)	α_c (mg/m²)
1	795	2	1.3	4.5	1.2
2	825	2	1.5	9.5	2.5
3	845	2	1.7	17.7	4.6

the surface with pyrolytic layers has properties similar to those of carbon adsorbents, but from the geometric and chemical points of view it is more heterogeneous than graphitized thermal or acetylene blacks.

B. Adsorption properties of pyrocarbon-modified silicas

To study the dependence of the adsorption properties of pyrocarbon adsorbents on the quantity of pyrocarbon applied to the surface of the silica carrier, samples of modified silica gel LiChrospher Si-500 ($S = 38 \text{ m}^2/\text{g}$) with 4.5, 9.5 and 17.7% (w/w) of pyrocarbon were investigated (Table V). Adsorption of water, benzene and hexane was studied.

The adsorption of water molecules having a clear-cut affinity for hydroxyl groups of the silica surface is a quite reliable method of probing modified surfaces and for assessing the extent of screening of silanol groups with a modifier. As the quantity of pyrocarbon on the silica gel surface in the initial region of the isotherms (Fig. 2) increased, the amount of water adsorbed gradually decreased. This is in accord with the reduction in the number of hydroxyl groups on the surface of these adsorbents that are accessible to water. Of interest is the marked change in the shape of the water adsorption isotherm on sample 3 (17.7%, w/w) as compared with the
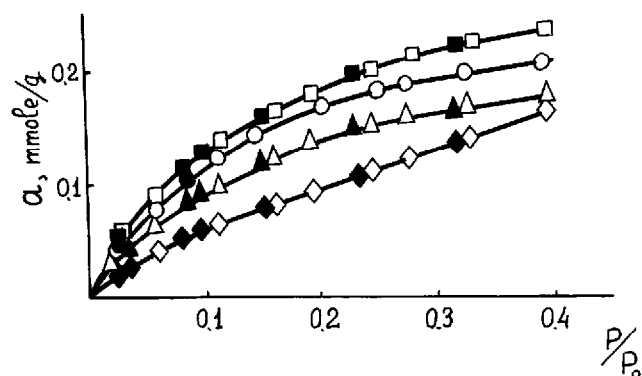

Fig. 2. Isotherms for water vapour adsorption at 25°C on the initial silica gel LiChrospher Si-500 (□) and silica gel modified by 4.5% (w/w) pyrocarbon (PC) (○); 9.6% (w/w) PC (△) and 17.7% (w/w) PC (◇). Filled symbols correspond to desorption.
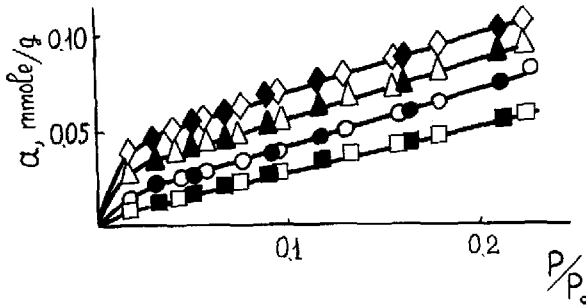
Fig. 3. Isotherms for *n*-hexane vapour adsorption at 25°C. Symbols as in Fig. 2.

initial sample and samples 1 and 2. Molecules on samples 1 and 2 seem to be adsorbed, mostly, on hydroxyl groups that are still accessible, but the number of such groups on the surface of sample 3 is negligible, therefore adsorption of water occurs chiefly on the pyrocarbon surface. This is manifested in an adsorption isotherm which tends to linearity. Thus, sample 3 does not only contain more pyrocarbon, but, probably, is characterized by a more uniform distribution of pyrolysis products on its surface.

The adsorption of hydrocarbons (hexane and benzene) on pyrocarbon adsorbents (Figs. 3 and 4) at values of $p/p_0 \leqslant 0.3$ occurs, on the whole, to a greater extent due to the much greater dispersion interaction energy of these molecules with new (carbon) centres and the higher concentration of such centres per unit surface area, as compared with that of hydroxyl groups on the initial silica gel.

The adsorption of benzene on the surface of sample 1 (4.5%, w/w pyrocarbon) is an exception. In this case, due to the low surface concentration of carbon ($\alpha_c = 1.2$ mg/m^2), the contribution of the dispersion energy is still insufficient to make up for the noticeable drop in the specific interaction energy of these molecules with
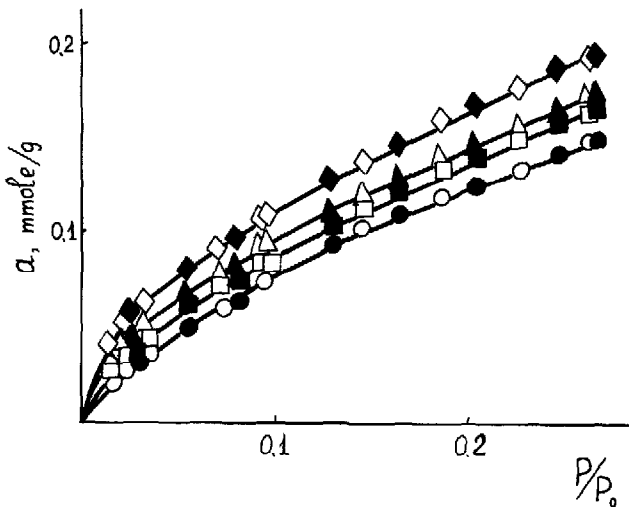

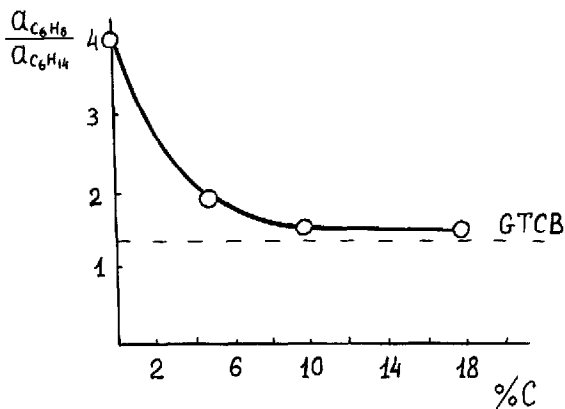Fig. 4. Isotherms for benzene vapour adsorption at 25°C. Symbols as in Fig. 2.

Fig. 5. Ratio of the adsorption of benzene and hexane, $a_{C_6H_6}/a_{C_6H_{14}}$, versus the quantity of pyrocarbon on the surface of silica gel LiChrospher Si-500 at $p/p_0 = 0.05$.

hydroxyl groups of the initial surface. In the case of sample 2, however, the benzene adsorption isotherm lies above that of the initial silica.

The ratio of the adsorption of benzene to that of hexane, $a_{C_6H_6}/a_{C_6H_{14}}$, versus the quantity of pyrocarbons on the silica gel surface (for $p/p_0 = 0.05$) in Fig. 5

TABLE VI

CAPACITY FACTORS FOR SOME AROMATIC HYDROCARBONS ON CARBOSILICA GEL

Column: 10 cm × 4.6 mm, LiChrospher Si-500 + 4.5% pyrocarbon. Mobile phase: methanol–water; flow-rate, 1 cm³/min. Temperature: 35°C.

Adsorbate	Methanol content of the mobile phase (%)		
	30	40	50
Benzene	1.18	0.89	0.79
Toluene	3.05	1.46	1.12
Ethylbenzene	5.49	2.03	1.44
Propylbenzene	14.29	4.32	2.90
Butylbenzene	39.68	9.83	5.78
Amylbenzene	–	–	11.12
Hexylbenzene	–	–	23.70
Cumene	–	–	1.84
tert.-Butylbenzene	–	–	2.40
o-Xylene	–	–	2.33
m-Xylene	7.82	–	2.12
p-Xylene	8.51	–	2.22
1,2,3-Trimethylbenzene	19.90	–	3.60
1,2,4-Trimethylbenzene	–	–	6.45
1,3,5-Trimethylbenzene	–	–	5.21
1,2,3,5-Tetramethylbenzene	–	–	7.49
Phenol	1.08	–	0.71
Anisole	2.52	–	1.12
Butyl phenyl ether	31.62	–	6.36

illustrates the reduction in the specificity of the surface of pyrocarbon-modified adsorbents. This ratio decreases from 4 in the case of the initial silica gel to 1.5 for a sample with 17.7% (w/w) of pyrocarbon. It is limited by the ratio of the capacities of the most non-specific and homogeneous surface, *i.e.*, graphitized thermal black[20] for dense monolayers of these hydrocarbons. This fact corroborates the uniform distribution of pyrocarbon on the surface of sample 3.

C. Liquid chromatography of substituted benzenes and non-substituted polyaromatic hydrocarbons on pyrocarbon adsorbents

The retention of alkyl- and methylbenzenes was studied on a column containing the modified sample of LiChrospher Si-500 with 5–10 μm particles and with 4.5% (w/w) pyrocarbon (sample 1 in Table V). Methanol–water mixtures (3:7, 2:3, 1:1) were used as eluents. The chromatographic peaks of the substances studied were
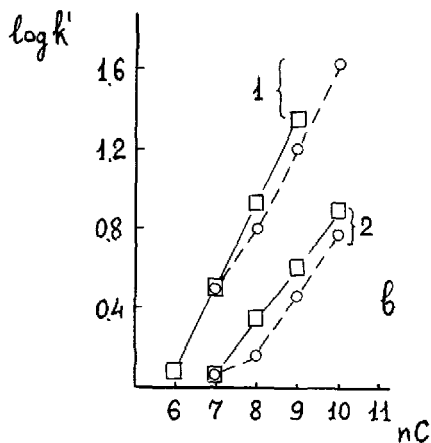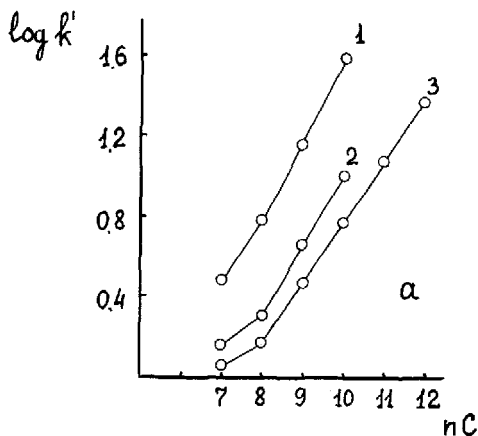

Fig. 6. Log k' as a function of n_c. (a) O—O, *n*-Alkylbenzenes on a pyrocarbon adsorbent (4.5%, w/w PC). Eluents: methanol–water 3:7 (1), 4:6 (2) and 1:1 (3). Temperature: 35°C. (b) □—□, Polymethylbenzenes on the same adsorbent. Eluents: methanol-water 3:7 (1) and 1:1 (2). Corresponding values for *n*-alkylbenzenes are shown by dashed lines.

sufficiently symmetrical and the retention time was independent of the sample volume. From Table VI it follows that, during elution with polar solvents, pyrocarbon adsorbents in liquid chromatography behave like the "reversed phase". Thus, for homologous series, the retention increases with increasing number of carbon atoms in the molecules (Fig. 6). A comparison of the retention of compounds having similar masses but comprising different functional groups shows that polar compounds are eluted before corresponding non-polar ones. Thus, phenol (MW = 94.1) emerges before toluene (MW = 92.1), anisole (MW = 108.2) before ethylbenzene (MW = 106.2) and butyl phenyl ether (MW = 150) before *n*-amylbenzene (MW = 148). As in case of conventional reversed-phase liquid chromatography (RPLC), the effect of the eluent is manifested quite vividly here in the decrease in retention time with the decrease in water content (lower polarity of the eluent).

However, there is also a considerable difference between the properties of the pyrocarbon adsorbent and "reversed phases", silicas with bonded alkyl groups. The chromatographic behaviour of substituted benzenes on the surface of the pyrocarbon adsorbent eluted with a polar eluent is similar to that found earlier in gas chromatography on GTCB[21] (Fig. 6b). Polymethylbenzenes are retained by the pyrocarbon surface more strongly than their isomeric alkylbenzenes. This confirms the difference in their geometric and electronic structures. Changes in the eluent composition do not alter this order of retention of substituted benzenes, although as the water content in the eluent increases from 50 to 70%, the difference in the retention of alkyl- and methylbenzene homologues with the equal carbon numbers, n_c, becomes less. Compared with the pyrocarbon in RPLC, the retention order of alkyl- and methylbenzenes is reversed on silica gel with bonded alkylsilyl groups at the same water concentrations[22–24]. Retention in liquid chromatography on pyrocarbon adsorbents seems to be determined only by the strong dispersion interactions of molecules of the substituted benzenes with the pyrocarbon-modified surface. This is verified by the fact that the dependences of the logarithm of the capacity factor, $\log k'$, on n_c have a bend at $n_c = 8$, as in gas chromatography on GTCB. This is associated with the possibility of free rotation of alkyl groups. Also of importance is the weaker (than on ordinary reversed phases) retention of isomers with branched alkyl radicals as compared with that of *n*-alkylbenzenes (Table VII). Finally, the order of elution of xylene isomers from pyrocarbon adsorbents in liquid chromatography is also similar

TABLE VII

RATIOS OF RETENTION VOLUMES OF ISOMERIC MOLECULES ON VARIOUS ADSORBENTS

$V'_{R_{(iso)}}/V'_{R_{(n-alkyl)}}$	Silica gels modified by:		
	Pyrocarbon	Alkylsilanes	
		$C_8{}^{22}$	$C_{22}{}^{22}$
Cumene/*n*-propylbenzene	0.63	0.83	0.83
tert.-Butylbenzene/ *n*-butylbenzene	0.41	0.70	0.66

TABLE VIII

CAPACITY FACTORS OF POLYAROMATIC HYDROCARBONS WITH ELUENTS OF VAR-
IOUS COMPOSITIONS

Column: 25 cm × 2 mm, LiChrospher Si-500 + 2.7% of pyrocarbon. Temperature: 29°C. Flow-rate: 0.6
cm³/min.

Polyaromatic hydrocarbon	Chloroform content in hexane (%)				
	0	20	50	70	100
Benzene	0.01	—	—	—	—
Naphthalene	0.19	0.07	0.05	0.04	0.04
Diphenyl	0.26	0.06	0.03	0.04	0.02
o-Terphenyl	0.22	0.05	0.02	—	—
m-Terphenyl	2.50	0.37	0.16	0.11	0.18
p-Terphenyl	3.83	0.67	0.28	0.18	0.13
Phenanthrene	14.68	1.99	1.27	0.74	0.62
Anthracene	—	2.27	1.58	0.87	0.65
Pyrene	—	9.63	4.56	2.94	2.12
2-Phenylphenanthrene	—	25.91	8.09	—	3.05
Triphenylene	—	—	10.81	6.65	4.18
Tetraphene	—	—	15.12	10.20	6.60
Chrysene	—	—	—	—	5.14
Triptycene	—	—	0.02	—	—

to that in gas chromatography on GTCB: m-xylene is the first to be eluted, followed
by the p- and o-isomers.

Thus, reversed-phase liquid chromatography of substituted benzenes on pyro-
carbon adsorbents is characterized by an adsorption mechanism of retention. In tra-
ditional RPLC it is the mobile phase that controls the retention, while the adsorbent
is less important. On pyrocarbon adsorbents, a particularly great rôle in the retention
is played by the geometric structure of the molecules adsorbed.

TABLE IX

CAPACITY FACTORS OF POLYAROMATIC HYDROCARBONS WITH ELUENTS OF VAR-
IOUS COMPOSITIONS

Column: 25 cm × 0.8 mm, LiChrospher Si-500 + 5.1% of pyrocarbon. Temperature: 22°C. Flow-rate:
60 µl/min.

Polyaromatic hydrocarbon	Chloroform composition in heptane (%)		
	0	5	25
Naphthalene	0.23	—	0.01
Phenanthrene	0.52	0.29	0.01
Pyrene	2.43	1.50	1.39
Triphenylene	7.63	4.46	3.58
Tetraphene	11.04	5.84	4.97

This is corroborated by data of the liquid chromatography of non-substituted polyaromatic hydrocarbons (PAHs) (Tables VIII and IX). Pyrocarbon adsorbents are capable of very strong non-specific (dispersion) interactions with molecules of PAHs and their retention increases greatly with increasing number of rings in the molecule. Thus, PAHs containing more than three aromatic rings are strongly retained ($k' > 10$) even when hexane and heptane are used as the eluents. Therefore, the eluents commonly used in RPLC, *i.e.*, water–alcohol and water–acetonitrile mixtures, cannot be utilized in liquid chromatography of PAHs on pyrocarbon adsorbents. For this purpose, it is advisable to add chloroform, which, according to Colin *et al.*[25], has the greatest effect on the elution of PAHs in liquid chromatography on pyrocarbon adsorbents. Chloroform is known to form π-complexes with the molecules of such compounds[26].

From Table VIII it follows that, just like GTCBs in GC pyrocarbon adsorbents are very sensitive to the geometric (three-dimensional) structure of the PAH molecule being adsorbed. Thus, non-planar molecules of terphenyls and triptycene are retained less strongly than those of anthracene and phenanthrene which contain fewer carbon atoms, but are flat. Similarly, 2-phenylphenanthrene (20 carbon atoms) is retained less strongly than triphenylene (18 atoms). Terphenyl isomers are eluted in the sequence *o*-, *m*- and *p*-terphenyl, as on GTCB in GC, due to the likely flat arrangement of the molecules on the adsorbent surface. The high sensitivity of pyrocarbon adsorbents to the geometry of the molecules being adsorbed helps in determining their three-dimensional structure from retention data in liquid chromatography.
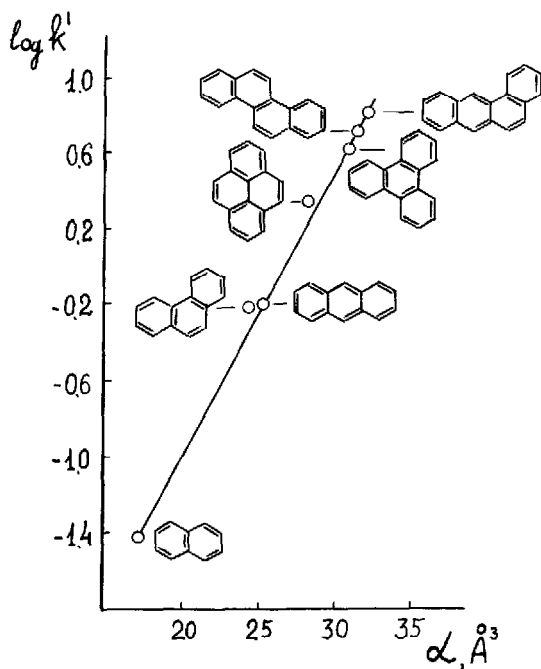

Fig. 7. Retention of non-substituted PAHs *versus* their molecular polarizability, α (Å^3)[27]. Column: 25 cm × 2 mm, LiChrospher Si-500 + 2.7% (w/w) PC. Eluent: chloroform.

From Tables VIII and IX it is seen that, upon elution with alkane–chloroform mixtures and with one non-polar solvent (hexane or heptane), the retention of isomeric PAHs corresponds to that observed in reversed-phase chromatography. Cata-condensed compounds annelated linearly are eluted later than their isomeric counterparts (cata-condensed compounds annelated angularly). Thus, anthracene is more strongly retained than phenanthrene and tetraphene more strongly than triphenylene. In direct liquid chromatography, on polar adsorbents, the elution order of isomeric PAHs is reversed. This demonstrates that during the adsorption of PAHs on pyrocarbon adsorbents from a non-polar solvent, specific interaction of PAH molecules with residual "polar" surface groups found, for example, in GC of polar molecules has little effect on the retention. Dispersion interactions are dominating for the retention of PAHs; this is corroborated by the similar elution order of isomeric PAHs in gas chromatography on GTCB[21,28,29].

A plot of the retention (log k) of PAHs *versus* their molecular polarizability is shown in Fig. 7. The almost linear dependence indicates the predominant dispersion interactions: polyaromatic hydrocarbon–adsorbent.

Thus, the properties of pyrocarbon adsorbents in liquid chromatography are similar to those of GTCB in gas chromatography. The high affinity of pyrocarbon adsorbents for aromatic hydrocarbons and their sensitivity to the geometry of such molecules contributes to the satisfactory separation of substituted aromatic hydrocarbons and PAH mixtures on low-efficiency columns.

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