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GAS CHROMATOGRAPHIC RETENTION ON CARBON ADSORBENTS COATED WITH MONOLAYERS OF POLYNUCLEAR AROMATIC HYDROCARBONS*

T. B. GAVRILOVA* and E. V. VLASENKO

Department of Chemistry, Lomonosov State University of Moscow, 119899 Moscow (U.S.S.R.)
and

N. PETSEV, I. TOPALOVA, Chr. DIMITROV and S. IVANOV

Department of Chemistry, Sofia University, 1126 Sofia (Bulgaria)

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SUMMARY

Monolayers of polynuclear aromatic hydrocarbons (PAHs) were used to modify carbon adsorbents (non-graphitized and graphitized thermal carbon blacks). The thermodynamic adsorption characteristics, retention volumes and initial differential heats of adsorption, of molecules belonging to different classes of organic compounds were measured by gas chromatography on these sorbents. The nature of the retention of molecules with different chemical properties on PAH-modified surfaces is determined predominantly by dispersion interaction by competing electrostatic interaction. The effect of PAH modification is the greatest on the retention of oxygen- and nitrogen-containing compounds. Exposure of thermal carbon blacks, modified with monomolecular PAH layers, to an high-frequency low-temperature plasma helps to improve the symmetry of chromatographic peaks.

INTRODUCTION

In order to extend the range of applications of gas-solid chromatography (GSC), homogeneous surface adsorbents are needed. Adsorbent surfaces can be made more homogeneous by a variety of methods, e.g., by application of monomolecular layers of organic molecules¹. Modification of carbon adsorbent surfaces with monomolecular layers of planar molecules, such as phthalocyanins of metals, 2,4,5,7-tetranitrofluorenal and pyrene and porphyrin derivatives, has demonstrated practically unlimited possibilities of producing adsorbents capable of both weak non-specific and strong specific interactions²⁻⁵.

When non-graphitized thermal carbon black, whose surface is chemically and geometrically heterogeneous⁶, is used as a support, the application of monolayers

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does not always lead to the desired results. The method of sorbent treatment with an high-frequency low-temperature plasma (HLP) helps greatly to improve the surface homogeneity^{7,8}.

In this work we have modified carbon adsorbents with molecules of various polynuclear aromatic hydrocarbons (PAHs) to study gas chromatographic (GC) retention. Changes in the surface properties of PAH-modified adsorbents exposed to HLP were analysed as well.

EXPERIMENTAL

Geometrically and chemically heterogeneous non-graphitized (TG-10) and graphitized thermal carbon blacks (GTCBs) with specific surface areas of 10 and 8 m²/g, respectively, were used as adsorbent supports. Planar PAH molecules, *viz.*, anthracene, pyrene, 1,2,5,6-dibenzanthracene and coronene having different electron densities, were used to modify the two adsorbents. The quantity of PAH adsorbed on the carbon black surface from a solution in benzene was calculated from the close packing of Van der Waal's radii of the modifier molecules, distributed over a planar surface, and using GC data². The quantity of modifier was adjusted so as to form a monomolecular layer and was equal to 0.4 mg/m² for anthracene and 0.6 mg/m² for pyrene, 1,2,5,6-dibenzanthracene and coronene.

The thermal carbon black TG-10, modified with pyrene and 1,2,5,6-dibenzanthracene, was additionally treated with HLP, as reported in ref. 8.

The retention volumes, V_g (per gram of adsorbent), relative retention volumes, $V_{rel} = V/V_{n-C_6H_{14}}$, and initial differential heats of adsorption, \bar{q}_1 , at low coverages of different classes of organic compounds. The initial of heats of adsorption were calculated from the slope of the linear dependence $\log V_g = f(1/T)$, where T is the column temperature.

The precision of the \bar{q}_1 values was evaluated statistically. The relative error was 0.5–1.0%.

Gas chromatographic measurements were made on a Tsvet-102 chromatograph equipped with a flame ionization detector and glass columns (0.5–1 m × 1.2 mm I.D.). The adsorbent particle size was 0.16–0.2 or 0.25–0.3 mm. Helium was used as the carrier gas (flow-rate 20–30 cm³ min⁻¹).

RESULTS AND DISCUSSION

The retention volumes of a variety of organic molecules, differing in both geometric and electronic structure, were determined on all adsorbents studied. A comparative study of the surface properties of adsorbents modified with PAH monolayers was carried out (Table I and Fig. 1). The data in Fig. 1 show that the retention volumes on GTCB with PAH monolayers are lower than in the case of pure GTCB. The greatest decrease in V_g occurs when coronene is used as the modifier. The V_g values of *n*-hydrocarbons on the modified surface are smaller due to the drop in adsorption potential caused by the decrease in the number of surface centres of force. The retention of aromatic hydrocarbons (Table I) on a GTCB surface coated with PAH is, probably, decreased in comparison with GTCB, due to repulsion between the π -electrons of the modified surface and the molecules adsorbed. This is seen most clearly when the relative retention volumes of hydrocarbon pairs with the same num-

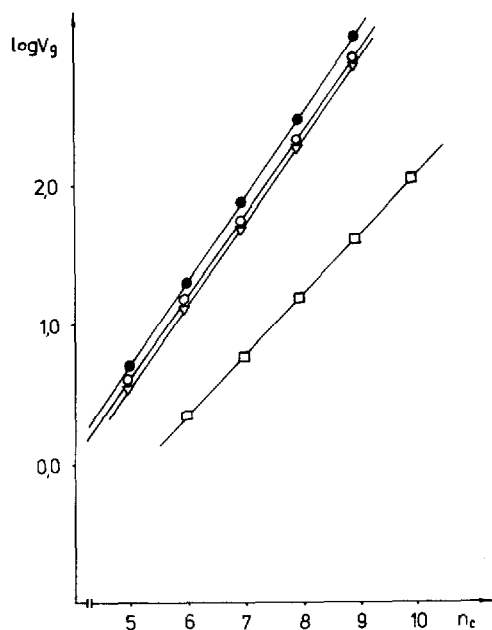


Fig. 1. Dependence of $\log V_g$ on the number of carbon atoms, n_c , of n -hydrocarbons on GTCB (●) and GTCB modified with monomolecular layers of anthracene (○), pyrene (▽) and coronene (□).

TABLE I

RELATIVE RETENTION VOLUMES, V_{rel} (WITH RESPECT TO n -HEXANE) AT 100°C ON UNMODIFIED GTCB AND ON GTCB MODIFIED WITH PAH MONOLAYER

Adsorbate	Unmodified GTCB	GTCB modified with monolayer of		
		Anthracene	Pyrene	Coronene
n -Heptane	3.9	3.7	3.6	2.5
Benzene	0.68	0.37	0.53	0.56
Toluene	4.1	1.6	2.4	1.8
p -Xylene	26	7.9	13	5.6
Propyl acetate	0.85	1.3	1.8	1.8
Di- n -propyl ester	1.8	—	2.1	2.0
n -Pentanol	0.89	1.3	3.1	1.9
Cyclohexane	0.04	0.45	0.69	0.65
Adamantane	2.4	7.7	8.4	9.0
Pyridazine	2.1	2.9	14	5.1
V_g of n -Hexane	20	15	14	2.3
V_g of Toluene	1.0	0.43	0.66	0.69
V_g of n -Heptane				
V_g of p -Xylene	1.8	0.57	0.92	0.82
V_g of n -Octane				

ber of carbon atoms are compared. For example, toluene and heptane, *p*-xylene and octane. The increase in relative retention volumes of adsorbates whose molecules possess polar functional groups indicates a greater contribution of specific interactions to the total adsorption energy than in the case with unmodified GTCB. There is probably a large increase in the electrostatic interactions involving the π -electron system of the modifying layer with adsorbed molecules whose electron density is localized on their periphery.

Compared with untreated carbon black, the pyrene-modified GTCB shows the most obvious increase in retention values for substances containing polar functional groups. At the same time, the retention values of *n*-alkanes are somewhat reduced (Table I). GTCB with a monomolecular coronene layer, displays the greatest decrease in retention of *n*-alkanes relative to unmodified GTCB, and the increase in the retention of polar compounds is somewhat less than in the case of GTCB with a pyrene monolayer. It is possible that the retention of molecules of different natures is affected, in this case, by competing contributions: a reduction in dispersion forces, on the one hand, and an increase in induction or electrostatic intermolecular interactions on PAH-modified adsorbents (unlike untreated GTCB) on the other hand. A significant reduction of the dispersion component may alleviate the effect of induction and electrostatic interactions.

The coefficients of $\log V_g = a + b_n$ for *n*-alkanes and *n*-alkylbenzenes were calculated for all adsorbents studied. Table II gives the values of *a* and *b* on untreated and PAH-modified carbon adsorbents and, for comparison, on a liquid phase, squalane in gas liquid chromatography⁹. GTCB and GTCB with a monomolecular anthracene or pyrene layer have almost identical contributions to the adsorption of the methylene group (coefficient *b*) on the adsorbent surface.

Although selectivity in homologous series of normal and aromatic hydrocarbons somewhat decreases when the initial carbon black is modified with PAH, it remains quite high, much higher than on squalane which is one of the most selective liquid phases for non-polar compounds.

When the PAH-modified non-graphitized thermal carbon black TG-10 is used as the adsorbent support, the changes in the retention of molecules belonging to

TABLE II

COEFFICIENTS IN $\log V_g = a + b_n$ AT 100°C FOR THE ADSORPTION OF *n*-ALKANES AND *n*-ALKYLBENZENES ON DIFFERENT ADSORBENTS

Adsorbent	<i>n</i> -Alkanes		<i>n</i> -Alkylbenzenes	
	<i>a</i>	<i>b</i>	<i>a</i>	<i>b</i>
GTCB	-2.22	0.59	-3.54	0.78
GTCB + anthracene	-2.24	0.57	-3.08	0.64
GTCB + pyrene	-2.26	0.58	-3.09	0.66
GTCB + coronene	-2.10	0.41	-2.68	0.47
TG-10	-2.34	0.65	-3.21	0.78
TG-10 + pyrene	-2.03	0.50	-2.68	0.55
TG-10 + 1,2,5,6-dibenzanthracene	-2.27	0.48	-2.85	0.54
Squalane ⁹	-0.35	0.32	-0.52	0.37

TABLE III

RELATIVE RETENTION VOLUMES, V_{rel} (WITH RESPECT TO *n*-HEXANE) AT 100°C ON UNMODIFIED AND MODIFIED THERMAL CARBON BLACK TG-10

<i>Adsorbate</i>	<i>Untreated TG-10</i>	<i>TG-10 treated with monolayer of</i>			
		<i>Pyrene</i>	<i>Pyrene and HLP</i>	<i>1,2,5,6-dibenz-anthracene</i>	<i>1,2,5,6-dibenz-anthracene and HLP</i>
Toluene	4.2	1.9	1.9	2.0	2.0
Diisopropyl ester	0.69	1.1	1.1	1.1	1.1
Ethyl acetate	0.61	1.1	0.90	0.95	0.92
Methyl ethyl ketone	0.50	0.96	0.67	0.70	0.67
<i>n</i> -Propanol	-	-	0.61	0.61	0.60
V_g of <i>n</i> -Hexane	40	9.2	4.6	4.1	3.8

different classes of organic compounds were the same as on GTCB (Tables I–III). When monomolecular PAH layers are applied, the decrease in V_{rel} is more apparent on TG-10 than on GTCB. Surface modification of TG-10 with PAH seems not only to decrease the adsorption potential, as is the case with GTCB, but also results in the blocking of additional adsorption centres on the TG-10 surface.

Samples of TG-10 with PAH monolayers were exposed to HLP. This treatment caused the retention of molecules of different compounds to decrease somewhat (Table III). The effect of exposure of the PAH-modified TG-10 to HLP is best seen from the shapes of the chromatographic peaks of substances whose molecules have the ability to undergo specific interactions with the adsorbent surface and therefore are sensitive to chemical and geometric heterogeneities of the adsorbent surface. Asymmetry factors measured at one-tenth peak height¹⁰ are shown in Table IV; exposure to HLP causes chromatographic peaks to become more symmetrical.

Greater symmetry of chromatographic peaks, as a result of exposure of the adsorbents investigated to HLP, indicates higher geometric and chemical surface homogeneity. A similar picture was observed earlier⁸ for diatomaceous earth coated with 5% squalane and then treated with an argon plasma.

TABLE IV

ASYMMETRY FACTORS¹⁰ OF PEAKS OBTAINED ON UNMODIFIED AND MODIFIED THERMAL CARBON BLACK AT 100°C

<i>Adsorbate</i>	<i>Untreated TG-10</i>	<i>TG-10 modified with monolayer of</i>			
		<i>Pyrene</i>	<i>1,2,5,6-dibenz-anthracene</i>	<i>Pyrene and HLP</i>	<i>1,2,5,6-dibenz-anthracene and HLP</i>
Adamantane	2.0	1.0	1.0	1.0	1.0
<i>p</i> -Xylene	3.6	1.5	1.0	1.0	1.0
<i>n</i> -Butanol	5.0	2.0	2.0	1.0	1.0
Pyridine	5.0	3.5	2.5	2.0	1.5

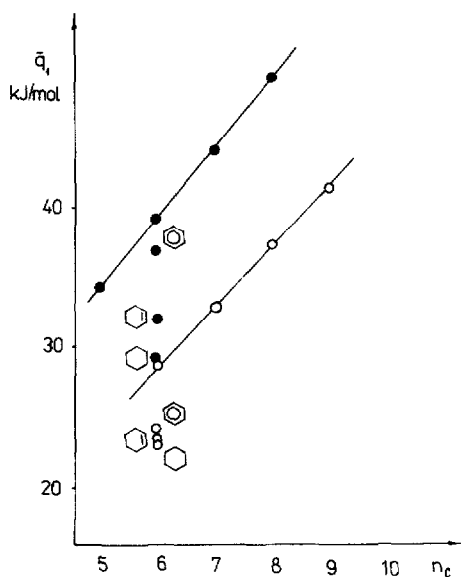


Fig. 2. Dependence of \bar{q}_1 on n_c in the adsorption of *n*-alkanes, cyclohexane, cyclohexene and benzene on GTCB (●)¹² and GTCB coated with a monolayer of coronene (○).

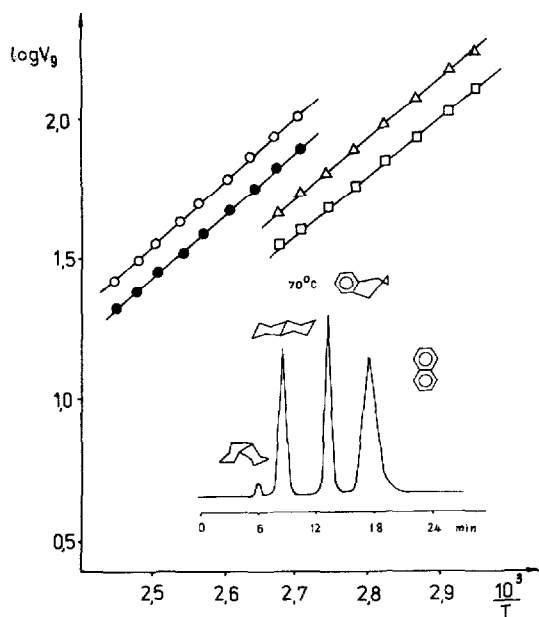


Fig. 3. Dependence of $\log V_g$ on $1/T$ for the adsorption of: □—□, *cis*-decalin; △—△, *trans*-decalin; ●—●, tetralin; ○—○, naphthalene on GTCB with a monolayer of coronene. The values of V_g are expressed in cm^3/g .

Coronene-modified GTCB was used to determine the initial heats of adsorption of some compounds. The influence of the electron density distribution in molecules adsorbing on the PAH-modified carbon black surface can be demonstrated. On the initial GTCB the \bar{q}_1 value for nitrobenzene is 59 kJ/mole; for aniline it is 54 kJ/mole¹¹. On the coronene-modified GTCB the corresponding values are 41 and 27 kJ/mole, respectively. On the latter adsorbent a greater reduction in the \bar{q}_1 values (27 kJ/mole) for aniline is observed than in the case of nitrobenzene (18 kJ/mole). This is due to the different effects of the $-\text{NO}_2$ and $-\text{NH}_2$ groups on the π -electron density of the benzene ring in the adsorbate molecules.

Fig. 2 shows the initial heats of adsorption of *n*-alkanes, cyclohexane, cyclohexene, and benzene on GTCB¹² and GTCB modified with coronene. Modifications reduces the \bar{q}_1 values for all hydrocarbons studied. Both adsorbents show an identical elution sequence of C₆ hydrocarbons which corresponds to the increase in energy of non-specific intermolecular interaction with the surface. However, the \bar{q}_1 values of hexane, benzene and cyclohexane, determined on GTCB coated with a coronene monolayer, are similar to each other, unlike the corresponding values for these compounds on unmodified GTCB.

Due to changes in the electronic structure of the carbon black surface, as a result of modification with coronene, the separation of naphthalene and its hydrogenated derivatives becomes possible on a packed column without temperature programming (Fig. 3), which is necessary when a GTCB column is used¹.

On PAH-modified adsorbents, various mixtures of organic compounds were separated. Fig. 4 shows a chromatogram of the separation of aliphatic alcohol isomers. A complete separation of butyl and amyl alcohol isomers and a partial separation of hexanol isomers was obtained. A mixture of methyl derivatives of phenol, isomers of *o*- and *m*-methylphenol and dimethylphenol, was separated isothermally (Fig. 5).

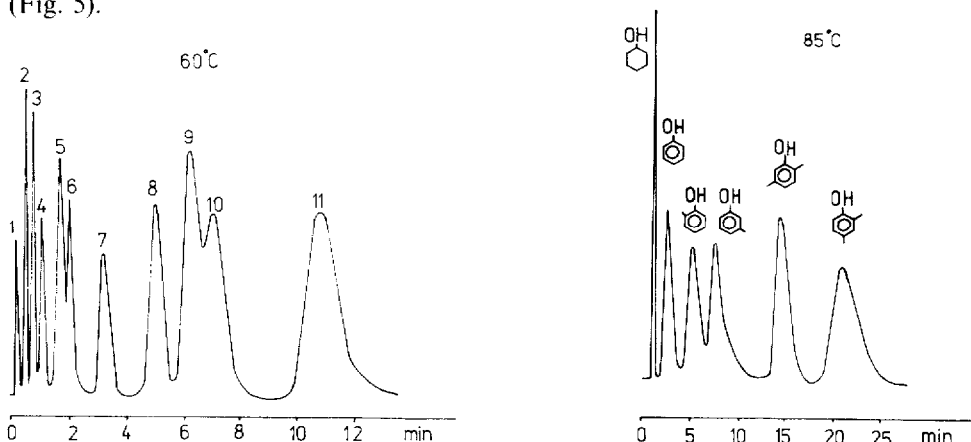


Fig. 4. Separation of a mixture of aliphatic alcohols on GTCB modified with coronene: 1 = ethanol; 2 = 2-methyl-2-propanol; 3 = 2-butanol; 4 = 1-butanol; 5 = 3-pentanol; 6 = 2-pentanol; 7 = 1-pentanol; 8 = 2-methyl-2-pentanol; 9 = 2-ethyl-1-butanol; 10 = 2-hexanol; 11 = 1-hexanol. Column: 70 cm \times 0.2 cm.

Fig. 5. Separation of methylphenols on GTCB modified with coronene: 1 = cyclohexanol; 2 = phenol; 3 = 2-methylphenol; 4 = 3-methylphenol; 5 = 2,5-dimethylphenol; 6 = 2,4-dimethylphenol. Column: 70 cm \times 0.2 cm.

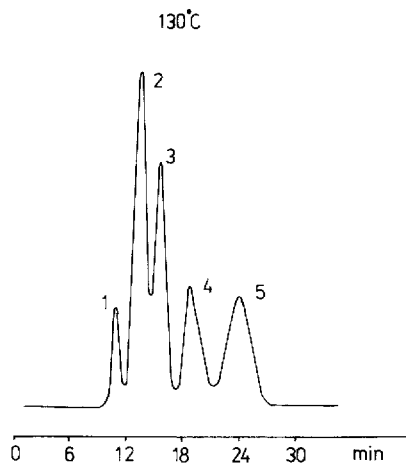


Fig. 6. Chromatograms of isomers of substituted pentanols and cyclohexanols on coronene-modified GTCB: 1 = 1-(3-methylbutyl)-1-cyclohexanol; 2 = 2-methyl-4-cyclohexyl-2-butanol; 3 = 1-cyclohexyl-2-pentanol; 4 = *cis*-2-pentyl-1-cyclohexanol; 5 = *trans*-2-pentyl-1-cyclohexanol. Column: 70 cm \times 0.2 cm.

Isomers of substituted pentanols and cyclohexanols, having the general formula $C_{11}H_{21}OH$, were separated (Fig. 6). The sequence in which the isomers emerge corresponds to their number of contacts with the adsorbent surface. For example, a straight-chain hydrocarbon radical in *ortho*-position with respect to the $-OH$ group, present in 2-pentyl-1-cyclohexanol, produces a maximum number of molecular contacts with the surface and this, therefore, results in the greatest retention; 2-pentyl-1-cyclohexanol shows two peaks, corresponding to the *cis*- and *trans*-isomers. The

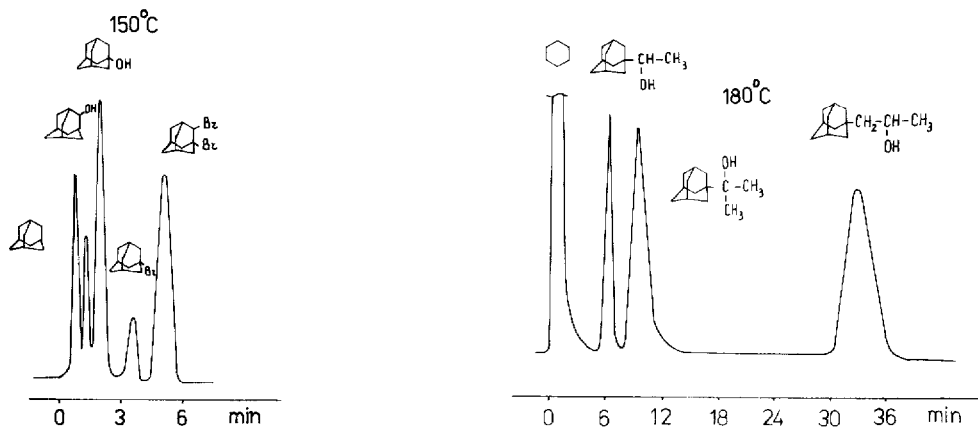


Fig. 7. Chromatogram of adamantane derivatives on GTCB modified with coronene: 1 = adamantane; 2 = 2-adamantanol; 3 = 3-adamantanol; 4 = 3-bromoadamantane; 5 = 2,3-dibromoadamantane. Column: 70 cm \times 0.2 cm.

Fig. 8. Chromatogram of adamantane derivatives on GTCB modified with coronene: 1 = cyclohexane; 2 = 3-adamantane-1-ethanol; 3 = 3-adamantane-1-isopropanol; 4 = 3-adamantane-2-propanol. Column: 70 cm \times 0.2 cm.

presence of a branched-chain hydrocarbon radical and an hydroxyl group on the carbon atom of 1-(3-methylbutyl)-1-cyclohexanol causes the retention of this compound to decrease considerably.

Figs. 7 and 8 show the separation of adamantane derivatives which are intermediate products in the synthesis of the biologically active, 2-adamantanamine. Both kinds of mixtures contain structural isomers that are well separated on the coronene-modified GTCB owing to differences in their geometric structures.

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