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CHROMATOGRAPHY OF AROMATIC HYDROCARBONS ON MACRO-POROUS POLYSTYRENE GEL

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SUMMARY

The chromatography of aromatic hydrocarbons on polystyrene gel was studied using water–methanol–diethyl ether as the eluent. The retention indices of a number of aromatic and alkylaromatic hydrocarbons are given. The influence of the number of carbon atoms and the position, shape and number of alkyl groups in the molecule is discussed.

INTRODUCTION

The adsorption chromatography of aromatic hydrocarbons on classical adsorbents (alumina and silica gel) has been extensively studied by many workers and general rules for the chromatographic behaviour of aromatic hydrocarbons and their alkyl derivatives have been formulated[1-3]. The use of classical adsorbents has some advantages, *e.g.*, the possibility of separating the saturated and aromatic portions of petroleum fractions and separating the aromatic fraction according to the number of aromatic rings in the molecule and good separation properties even at high loadings. These properties have led to their wide use in the analysis of natural hydrocarbon mixtures. In addition to these adsorbents, increasing analytical use is being made of liquid–liquid chromatographic packings, which are commercially available from many companies. Except for a limited number of instances, these types of chromatographic packings have not been used in studies of the chromatography of aromatic hydrocarbons. In general, these packings cannot be used for the selective separation of saturated and aromatic hydrocarbons but, in contrast, they are widely used in the analysis of organic compounds that contain different functional groups or heteroatoms.

An example of the separation of aromatic and alkylaromatic hydrocarbons in the so-called reversed phase system is the work of Sleight[4], who separated them by

using Zipax Permaphase ODS with water–methanol as the eluent. He showed that the elution volumes of aromatic hydrocarbons increased with an increase in the number of carbon atoms in the molecule. A similar effect was found with alkyl derivatives. The relationship

$$\log k' = a + bC \tag{1}$$

where k' is the capacity factor, a and b are constants, and C is the number of carbon atoms in the molecule is generally valid. Typical values of a and b are given in Table I.

The constant b, which is the slope of the straight-line graph of log k' *versus* C, is larger for alkylnaphthalenes and alkylphenanthrenes than for the parent hydrocarbons, so that in practice that possibilities of using this system are limited to the analysis of aromatic hydrocarbons with a certain number of rings in the molecule. When applying to the column a mixture of a wide range of highly alkylated aromatic hydrocarbons with a varying number of rings in their molecules, it may happen that hydrocarbons that differ not only in the number of alkyl carbons but also in the number of aromatic rings will be eluted simultaneously.

TABLE I

VALUES OF THE CONSTANTS a AND b IN EQN. 1

Compound type	a	b
Parent aromatic hydrocarbons	−1.74	0.109
Alkylbenzenes	−8.83	0.100
Alkylnaphthalenes	−0.63	0.129
Alkylphenanthrenes	−0.25	0.161

This paper deals with the behaviour of aromatic hydrocarbons and their derivatives during their chromatographic separation on a gel of the cross-linked polystyrene type prepared in the Research and Development Department of Laboratory Instruments N.E. (Laboratorní Přístroje), Prague. This material, in contrast to most commercial packings of this type, does not form a pellicular layer on the support but consists of completely porous spherical particles.

Alkylaromatic hydrocarbons, cyclanoaromatic hydrocarbons and diphenylalkanes were also studied, in addition to a number of parent aromatic hydrocarbons. The results obtained are presented in the form of retention indices[3].

EXPERIMENTAL

The packing was a cross-linked polystyrene gel with spherical particles of size 25–32 μm and an exclusion limit of mol.wt. 40,000. Thick-walled glass columns of dimensions 500 × 3, 300 × 4 and 150 × 4 mm were used. The eluent was water–diethyl ether–methanol (11:18:71, by volume). The pump was an ISCO Dialagrad Model 384 with pulseless delivery of the solvent in the range 0.5–160 ml/h, with a maximum pressure of 200 kp/cm². A UV detector with variable wavelength (200–400 nm), equipped with a cell with an optical path length of 10 mm and dead volume 10 μl (Development Works of the Czechoslovak Academy of Sciences, Prague) was used.

Procedure

The columns were packed with a suspension of the gel in methanol. The column was compressed at a pressure of 25–30 kp/cm^2 and the packing was completed stepwise. A procedure based on packing the column with a suspension in methanol under flow conditions and dry packing by using vibrations along the longitudinal axis of the column were also tested. The greatest efficiency was achieved when the column was packed stepwise with the suspension in methanol; the dry-packed columns exhibited the lowest efficiency. The efficiency of the columns packed stepwise with the suspension in methanol expressed as the HETP can be seen from Fig. 1.

The effect of temperature on the elution times and capacity factors was tested in the range 21–66°.

In addition to a series of parent aromatic hydrocarbons, the elution data of monoalkyl derivatives were measured and, for benzene, also for polymethyl derivatives. A series of cyclanobenzenes and diphenylalkanes was also studied.

RESULTS AND DISCUSSION

Efficiency of the separation system

The dependence of the measured HETP values (H mm) on the linear velocity of the eluent (u mm/sec) is shown in Fig. 1. The efficiency of the gel appeared to be remarkably high. At velocities of about 5 mm/sec, the highest values of H were about 1 mm. The efficiency is affected by the internal diameter of the column, whereas the column length has only a slight effect on H. The dependences in Fig. 1 were calculated for compounds with relative high capacity factors (for naphthalene $k' = 4.2$).
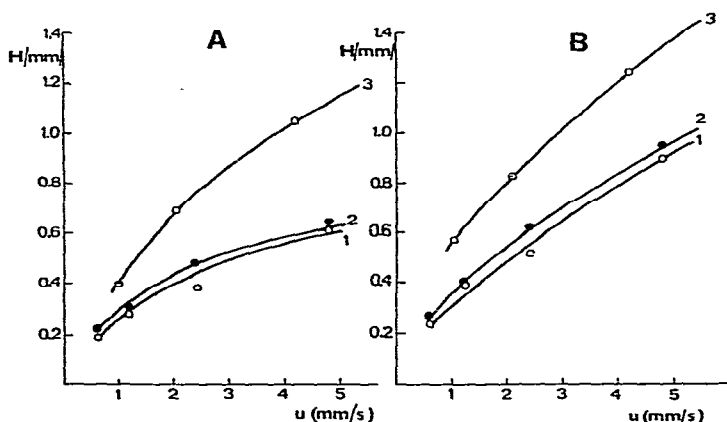

Fig. 1. HETP *versus* linear eluent velocity, u. Testing solutes: A, naphthalene, $k' = 4.2$; B, phenanthrene, $k' = 8.9$. Column: 1, 150 × 4 mm; 2, 300 × 4 mm; 3, 500 × 3 mm.

The separation of aromatic hydrocarbons on the polystyrene gel can be considered as partition chromatography. This is supported by results obtained by measuring capacity factors at four different temperatures in the range 21–66° (Fig. 2). A temperature increase of 45° resulted in a decrease in k' of about 50%. A similar effect was reported by Schmit *et al.*[5], who deserved that an increase in temperature of
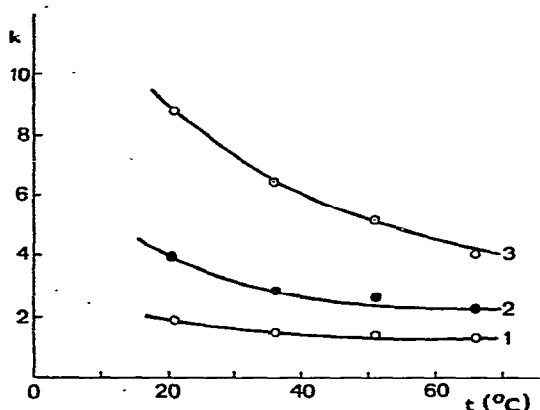
Fig. 2. Dependence of k' on temperature. Column, 500 × 3 mm. Curves: 1 = benzene; 2 = naphthalene; 3 = phenanthrene.

30° led to a decrease in k' of 50 %. This is an important feature of the partition chromatography process, where temperature plays a major role, in contrast to adsorption chromatography[6].

Chromatographic separation of aromatic and alkylaromatic hydrocarbons

The elution data measured are presented as logarithms of retention index (Table II) calculated according to a previously proposed procedure[3], and are shown graphically in Figs. 3–5. The dependence of the value of log I on the total number of carbon atoms in a molecule is linear (Fig. 6) in all of the series studied and can be described generally by the equation

$$\log I = \alpha + \beta N_C \tag{2}$$

where α and β are constants and N_C is the number of carbons in the molecule. The values of α and β, calculated by linear regression from the experimental data, are given in Table III. This table indicates that the slopes β for n-alkyl derivatives decrease with increasing number of rings in the basic hydrocarbon, so that the average contribution of an alkyl carbon atom, log I, decreases with increasing number of rings in the hydrocarbon. The effect of alkyl branching, which is similar to that encountered in the adsorption chromatographic separation of alkylaromatic hydrocarbons on alumina[1,2], is of interest. However, it seems, as can be seen from Table II, that the site of the branching (in a given case the α-carbon with respect to the ring) is not a significant factor that could affect the hydrocarbon elution volume. A comparison of the elution data for neopentylbenzene, 2-phenylpentane, 3-phenylpentane, isobutylbenzene and *sec.*-butylbenzene suggests that the site of the branching and the shape of the alkyl group do not greatly affect the alkylbenzene elution volume.

More significant differences in the elution volumes were observed when comparing the elution data of mono-n-alkylbenzenes and the corresponding polymethylbenzenes (Fig. 4).

The elution volumes of the polymethylbenzenes were very similar to those

TABLE II

ELUTION DATA FOR DIFFERENT TYPES OF AROMATIC HYDROCARBONS

Type	Compound	Log I	Carbon number
Parent aromatic hydrocarbons	Benzene	1.000	6
	Naphthalene	2.000	10
	Diphenylene	2.379	12
	Phenanthrene	3.000	14
	Anthracene	3.086	14
	Pyrene	3.450	16
	Fluoranthene	3.365	16
	1,2-Benzanthracene	4.000	18
	Chrysene	3.946	18
	Perylene	4.628	20
Alkylbenzenes	Toluene	1.224	7
	o-Xylene	1.344	8
	m-Xylene	1.322	8
	p-Xylene	1.322	8
	n-Propylbenzene	1.441	9
	Isopropylbenzene	1.411	9
	1,2,4-Trimethyl benzene	1.597	9
	1,3,5-Trimethylbenzene	1.565	9
	n-Butylbenzene	1.638	10
	1,2,4,5-Tetramethylbenzene	1.852	10
	Isobutylbenzene	1.518	10
	sec.-Butylbenzene	1.431	10
	n-Amylbenzene	1.810	11
	2-Phenylpentane	1.657	11
	3-Phenylpentane	1.623	11
	Neopentylbenzene	1.687	11
	Hexamethylbenzene	2.268	12
	1-n-Propyl-2,3,4-trimethylbenzene	2.079	12
	m-Diisopropylbenzene	1.638	12
	n-Heptylbenzene	2.238	13
	4-Phenylheptane	1.950	13
	n-Octylbenzene	2.337	14
	n-Decylbenzene	2.697	16
	Hexaethylbenzene	3.578	18
Alkylnaphthalenes	1-Methylnaphthalene	2.245	11
	2-Methylnaphthalene	2.251	11
	1-Ethylnaphthalene	2.317	12
	2-Ethylnaphthalene	2.315	12
	1-n-Propylnaphthalene	2.525	13
	1-Isopropylnaphthalene	2.355	13
	1-n-Amylnaphthalene	2.798	15
	1-(3-Amyl)naphthalene	2.555	15
Alkylphenanthrenes	9-Methylphenanthrene	3.194	15
	9-Ethylphenanthrene	3.245	16
	9-n-Propylphenanthrene	3.382	17
	9-Isopropylphenanthrene	3.309	17
	9-n-Amylphenanthrene	3.750	18
	9-(3-Amyl)phenanthrene	3.359	18

TABLE II (*continued*)

Type	Compound	Log I	Carbon number
Cyclanobenzenes	Indane	1.740	9
	Tetralin	2.038	10
	2a,3,4,5-Tetrahydroacenaphthene	2.384	12
	1,2,3,4,5,6,7,8-Octahydroanthracene	2.977	14
	1,2,3,4,5,6,7,8-Octahydrophenanthrene	3.013	14
	1,2,3,4,4a,9,10,10a-Octahydro-phenanthrene	2.889	14
	1,2,3,3a,4,5,5a,6,7,8-Decahydropyrene	3.194	16
	1,2,2a,3,4,5,6,6a,9,10,11,12-Dodecahydrochrysene	3.628	18
	1,2,3,4,4a,5,6,7,8,9,9a,10,11,12-Tetradecahydroperylene	4.032	20
Diphenylalkanes	Diphenylmethane	2.327	13
	1,1-Diphenylethane	1.992	14
	1,2-Diphenylethane	2.483	14
	1,4-Diphenylbutane	2.881	16
	1,6-Diphenylhexane	3.282	18
Others	6-Methyltetralin	2.198	11
	1,4-Dimethylindane	2.007	11
	Biphenyl	2.255	12
	Acenaphthene	2.577	12
	Acenaphthylene	2.419	12
	Fluorene	2.702	13
	1-Methylfluorene	2.934	14
	9-Methylfluorene	1.412	14
	9,10-Dihydroanthracene	2.697	14
	9,10-Dihydrophenanthrene	2.888	14
	1,2,3,4-Tetrahydroanthracene	2.987	14
	1,2,3,4-Tetrahydrophenanthrene	2.980	14
	cis-Stilbene	2.587	14
	trans-Stilbene	2.872	14
	1,2:4,5-Dibenzocycloheptane	2.466	15
	1,2:5,6-Dibenzocyclooctane	3.298	16
	4,5-Dihydropyrene	3.401	16
	4,5,9,10-Tetrahydropyrene	3.276	16
	o-Terphenyl	2.995	18
	m-Terphenyl	3.754	18
	p-Terphenyl	3.656	18

corresponding to the series of parent aromatic hydrocarbons. When one or more alkyl groups higher than methyl are present in the molecule, then the elution volume of the hydrocarbons decreases (*e.g.*, 1-*n*-propyl-2,3,4-trimethylbenzene). One can assume that the area bounded by the straight lines for the polymethylbenzenes (upper limit) and isoalkylbenzenes (lower limit) (Fig. 4) represents a region that will include data for most mono- and polyalkylbenzene derivatives.

For monoalkylnaphthalenes and monoalkylphenanthrenes, dependences similar to those for alkylbenzenes were found. The non-equivalence of individual alkyl positions that had a considerable effect on the elution volumes of alkylaromatic
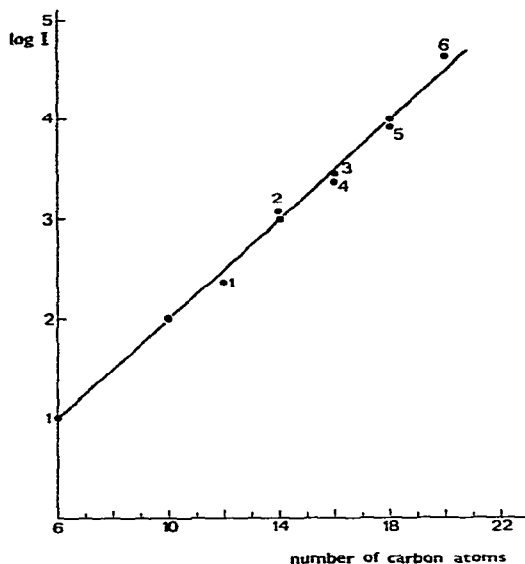
Fig. 3. Log *I* *versus* number of aromatic carbon atoms in the molecule. Fused parent aromatics. 1, Diphenylene; 2, anthracene; 3, pyrene; 4, fluoranthene; 5 chrysene; 6, perylene. Values of log *I* for benzene, naphthalene, phenanthrene and benz(a)anthracene are defined as 1.000, 2.000, 3.000 and 4.000, respectively.
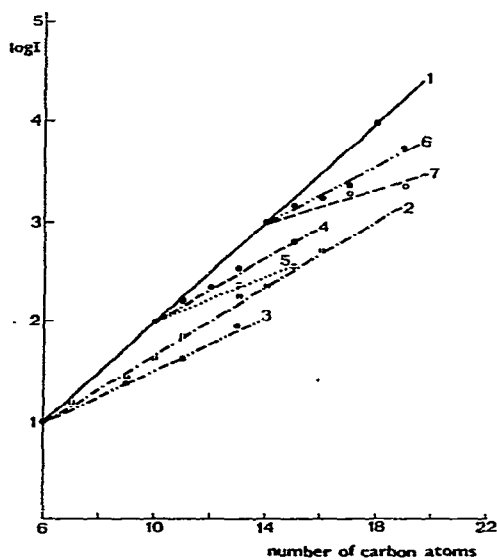

Fig. 4. Log *I* versus number of carbon atoms in the molecule. Curves: 1, parent aromatic hydrocarbons; 2, *n*-alkylbenzenes; 3, isoalkylbenzenes; 4, *n*-alkylnaphthalenes; 5, isoalkylnaphthalenes; 6, *n*-alkylphenanthrenes; 7, isoalkylphenanthrenes.
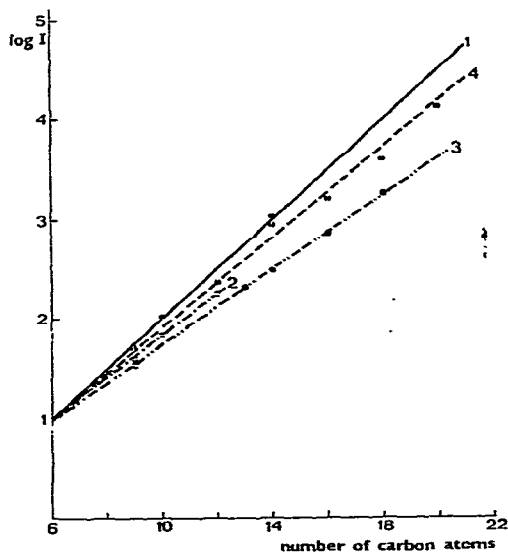
Fig. 5. Log *I* versus number of carbon atoms in the molecule. Curves: 1, parent aromatic hydrocarbons; 2, polymethylbenzenes; 3, (α,ω)-diphenylalkanes; 4, cyclanobenzenes.

TABLE III

VALUES OF THE CONSTANTS α AND β IN EQN. 2

Group	α	β
Parent aromatic hydrocarbons	—0.500	0.250
n-Alkylbenzenes	—0.024	0.170
Isoalkylbenzenes	0.199	0.133
Polymethylbenzenes	—0.394	0.220
n-Alkylnaphthalenes	0.484	0.155
Isoalkylnaphthalenes	0.890	0.111
n-Alkylphenanthrenes	0.990	0.144
Isoalkylphenanthrenes	1.985	0.074
Cyclanobenzenes	—0.160	0.214
Diphenylalkanes	—0.142	0.189

hydrocarbons in chromatographic separations on alumina and silica gel[2] was not observed in this instance. Thus, the separation achieved depends only on the number of carbon atoms in the alkyl group.

The contribution corresponding to a carbon atom in an n-alkyl group, $\Delta \log I$, is always lower than the value of $\Delta \log I$ corresponding to an aromatic carbon atom. In addition, an average contribution from one carbon atom of an n-alkyl group decreases with increasing number of rings in the parent aromatic hydrocarbon. The contribution from the cyclanic carbon atom, or the effect of the cyclane ring in the molecule, cannot be characterized as unambiguously. The elution data for all cyclanobenzenes with a maximum of 14 carbon atoms correspond closely to the values measured for the relevant completely aromatic molecule. However, the values of log I for decahydropyrene, dodecahydrochrysene and tetradecahydroperylene are very different from those for parent aromatic hydrocarbons. It seems probable that this
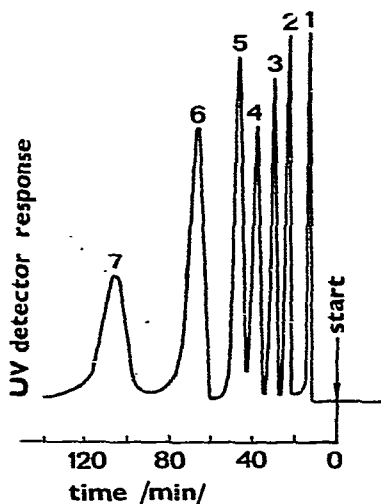

Fig. 6. Separation of parent aromatic hydrocarbons. Peaks: 1, benzene; 2, naphthalene; 3, diphenylene; 4, fluorene; 5, phenanthrene; 6, pyrene; 7, benz(a)anthracene.

difference does not result from subjective effects (measurement errors or fluctuations of temperature, flow-rate or eluent composition) and thus the data measured may be considered as sufficiently precise for the hydrocarbons of interest. One can assume from these data that the value of the retention index for a cyclanobenzene decreases absolutely as well as relatively with respect to the value corresponding to the completely aromatic hydrocarbon with an increasing number of carbon atoms in the hydrocarbon molecule.

The diphenylalkanes can be considered as substituted benzenes. In the course of the linear correlation of the data measured, benzene was also included with very good results (Table III; Fig. 5). In this group, an exception is 1,1-diphenylethane, the retention index of which is lower than those for diphenylmethane and 1,2-diphenylethane. Similar anomalous behaviour was observed with 9-methylfluorene, whereas the retention index of 1-methylfluorene corresponded closely to the predicted value (Table II). At present it is difficult to offer a satisfactory explanation for this phenomenon.

There are several hydrocarbons that were not included in the above groups but which show interesting behaviour. Thus, the retention index of o-terphenyl is much lower than those of the m- and p-isomers and corresponds to the values for C_{14} fused aromatic hydrocarbons. When considering the separation system described as partition chromatography, it is impossible to attribute the above difference in the values of I to the different steric arrangements of the molecules. Under this assumption, the anomalous phenomena observed can be attributed to the extremely low distribution coefficients of these compounds, $i.e.$, to their relatively higher affinity for the mobile phase. However, this hypothesis was not tested with any physical data on these compounds. The existence of compounds that differ in their distribution coefficients owing to the different steric arrangements of their molecules is very likely. Similar, although smaller, differences were observed with stilbenes (Table II), where the value of I for the cis-isomer was lower. On the contrary, the elution data for the pair diphenyl–diphenylene demonstrate that the explanation of the anomalous behaviour of certain compounds in terms of steric effects could not be satisfactory. In the chromatography on a macroporous polymer, it is possible to consider the existence of adsorption phenomena that can be mutually complementary with the process of dissolution of the compound to be separated in the polymer. Then, the resulting effect of the two different mechanisms depends on the individual contributions of each. In order to draw more accurate conclusions, it will be necessary to study in more detail the character of the surface of the polymer used and its interactions with model substances in terms of the physical parameters that affect the sorption.

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