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## CHROMATOGRAPHIC BEHAVIOUR OF AROMATIC HYDROCARBONS AND HETEROCYCLIC COMPOUNDS ON SILICA GEL WITH A CHEMICALLY BONDED AMINO PHASE

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The chromatographic behaviour of a series of polycyclic aromatic hydrocarbons and heterocyclic compounds was investigated on Separon SIX NH<sub>2</sub>, a sorbent with chemically bonded amino groups. The effect of substitution and partial hydrogenation of the aromatics on their retention was examined. The achieved separation of aromatic hydrocarbons from their mixtures into groups, each containing substances with the same number of rings, was compared with that published for other, similar chromatographic materials. The effect of structure of some heterocyclic compounds on their affinity for the stationary phase, in comparison with the related aromatic hydrocarbons, is also discussed.

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Hydrocarbon mixtures can be conveniently separated by liquid chromatography on highly efficient packings with chemically bonded stationary phases, usually of hydrocarbon type<sup>1</sup>. A type of material which is finding increasing use for this purpose is the so-called "amino phases", sorbents chemically modified by compounds containing amino group. Combined with pure saturated hydrocarbon eluents such as pentane or hexane, these sorbents enable aromatic hydrocarbon mixtures to be separated into groups of compounds with the same number of aromatic rings in their molecules<sup>2-6</sup>. In some cases the elution strength of the mobile phase has to be increased by addition of a suitable modifier<sup>4,5</sup>.

Conventionally, such separations are carried out on columns packed for one use with combinations of silica gel and aluminium oxide; a series of eluents of increasing polarity is employed<sup>7,8</sup>.

In the present work, the chromatographic behaviour of aromatic hydrocarbons and heterocyclic compounds is studied on microparticulate silica gel with chemically bonded amino groups. The effect of the aromatics structure on the retention is examined, the separation of aromatic hydrocarbons into groups with identical numbers of rings is followed, and the differences in the retention of aromatics and related heterocyclic compounds are evaluated.

## EXPERIMENTAL

Amino silica gel Separon SIX NH<sub>2</sub> (particle size 5  $\mu\text{m}$ ) furnished by the manufacturer (Laboratorní přístroje, Prague) in a CGC glass column 150 mm long, 3.2 mm i.d. The eluents, hexane (Reakhim, USSR) and 2-propanol (Lachema, Brno), were used without additional pretreatment.

The liquid chromatography system comprised an HPP 4001 pump (Laboratorní přístroje, Prague), an LC 3 UV detector (Pye Unicam, Cambridge), a Model 7125 sample loop (Rheodyne, USA), and a DP 88 integrator (Pye Unicam, Cambridge).

Standards were injected in 0.5–7  $\mu\text{l}$  volumes of 0.01–0.1% solutions in hexane. The eluent flow rate was 0.5  $\text{ml min}^{-1}$ . The detection wavelengths coincided with the characteristic UV absorption maxima. The retention times were recorded by the integrator; the data given in Table II are averages of eight measurements.

## RESULTS AND DISCUSSION

One of the purposes of this work was to examine the effect of the differences in the structure of aromatic hydrocarbons with the same number of aromatic rings on their chromatographic behaviour on the sorbent modified by amino phase. The affinity of the compounds for the stationary phase was characterized by their capacity ratios ( $k$ ) and retention indices ( $I_x$ ) introduced by Popl and coworkers<sup>9</sup>. The reference  $I_x$  values, requisite for the calculations, are given in Table I.

Table II gives the capacity ratios, their standard deviations, and logarithms of the calculated retention indices for a series of aromatic hydrocarbons. Monoaromatic hydrocarbons elute up to  $\log I_x = 1.5$ . For diaromatic hydrocarbons,  $\log I_x \approx 1.7$ – $2.5$ ; for triaromatic hydrocarbons,  $\log I_x \approx 2.5$ – $3.5$ ; and for tetraaromatic hydrocarbons,  $\log I_x \approx 3.8$ – $4.0$ . Hydrocarbons with five cycles and more elute at  $\log I_x > 4.1$ .

The retention indices are not lowered appreciably by substitution by methyl groups in the molecules; for hexamethylbenzene this value is even higher than for the parent hydrocarbon. Cycloaromatics also elute within the corresponding limits, with slightly enhanced  $I_x$  values except for dimethyldihydrophenanthrene. The decrease

TABLE I  
Reference retention indices of aromatic hydrocarbons

Compound	$\log I_x$
Benzene	1
Naphthalene	2
Phenanthrene	3
Benz( <i>a</i> )anthracene	4
Dibenz( <i>a,h</i> )anthracene	5

TABLE II

Capacity ratios ( $k$ ), their standard deviations ( $s$ ), and logarithms of retention indices ( $\log I_x$ ) of aromatic hydrocarbons

Compound	$k^a$	$s \cdot 10^3$ <sup>a</sup>	$\log I_x$
Benzene	0.087	2.864	1.000
1,3,5-Trimethylbenzene	0.074	1.900	< 1.000
Hexamethylbenzene	0.166	1.814	1.490
Dodecylbenzene	0.065	1.900	< 1.000
Dodecahydrochrysene	0.127	3.326	1.286
Tetradecahydroperylene	0.167	1.814	1.494
Naphthalene	0.325	2.864	2.000
Biphenyl	0.343	1.814	2.062
1-Methylnaphthalene	0.354	2.192	2.099
1,5-Dimethylnaphthalene	0.262	1.900	1.836
2,6-Dimethylnaphthalene	0.322	1.587	1.993
1-Propylnaphthalene	0.237	2.192	1.760
Acenaphthene	0.315	4.611	1.975
Fluorene	0.523	1.192	2.554
4,5-Dimethyl-9,10-dihydrophenanthrene	0.278	3.704	1.881
1,2,3,4-Tetrahydrofluoranthene	0.496	0.680	2.492
1,2,3,3a,4,5-Hexahydropyrene	0.475	1.209	2.442
Phenanthrene	0.676	1.587	3.000
2-Phenylnaphthalene	0.796	0.000	3.050
Benzo[b]fluorene	1.050	3.099	3.416
Anthracene	0.763	2.864	2.995
9,10-Dimethylantracene	0.697	1.209	2.859
9-Methylphenanthrene	0.712	3.099	2.914
4,5-Dimethylphenanthrene	0.730	1.587	2.943
4,5-Methylenphenanthrene	0.665	1.209	2.834
9-Ethylphenanthrene	0.637	1.814	2.784
9-Propylphenanthrene	0.602	6.425	2.718
9-Amylphenanthrene	0.556	1.209	2.625
9-Dodecylphenanthrene	0.498	1.209	2.497
2-Dodecylphenanthrene	0.499	1.587	2.499
Fluoranthene	1.046	4.238	3.411
9-Phenylantracene	1.250	0.000	3.697
Benz[a]anthracene	1.633	3.023	4.000
Pyrene	0.990	6.349	3.334
1-Methylpyrene	0.954	1.209	3.289
Chrysene	1.717	1.814	4.066
Dibenz[a,c]anthracene	3.197	3.023	4.875
Dibenz[a,h]anthracene	3.519	1.587	5.000
Benzo[a]pyrene	2.225	2.721	4.403
Picene	3.657	1.814	> 5.000

TABLE II  
(Continued)

Compound	$k^a$	$s \cdot 10^3$ <sup>a</sup>	$\log I_x$
Perylene	2.446	1.900	4.526
3-Hexylperylene	1.789	0.587	4.119
Benzo[ <i>g,h,i</i> ]perylene	2.850	3.023	4.725
Coronene	3.423	2.842	4.964

<sup>a</sup> Calculated from eight replicate measurements.

in the retention index value is more marked for aromatics with a long alkyl chain substituent. In addition to the two dodecylphenanthrenes, fluorene and benzo(*b*)-fluorene are on the boundaries of the corresponding groups; the two hydrogen atoms in positions 9 and 10 appear to play a role. For fluoranthene, pyrene, and methylpyrene, the  $I_x$  value even overlap; however, it should be borne in mind that actually the formally tetranuclear pyrene is isomeric with fluoranthene. As to polynuclear aromatic hydrocarbons, their  $k$  and  $I_x$  values are influenced by the shape of their molecules.

High-boiling hydrocarbon mixtures of petroleum or coal origin also contain sulphur, nitrogen, and oxygen heterocyclic compounds of aromatic nature. The chromatographic behaviour of some compounds of this type is demonstrated by Table III. While the oxygen and sulphur analogues exhibit  $k$  values not very different from those of the corresponding aromatic hydrocarbons, for the nitrogen compounds these values differ as much as an order of magnitude; this applies also to pyridine and indole. This effect can be explained in terms of a strong interaction between the amino groups of the stationary phase and the nitrogen atom of the heterocyclic compound. This interaction is additionally enhanced by the presence of the protic hydrogen bonded to nitrogen in the molecule of indole.

The effect of structure of nitrogen heterocycles on their chromatographic behaviour is shown, for some typical substances, in Table IV. The eluent used was a hexane-2-propanol 99 : 1 mixture. For compounds containing a protic hydrogen bonded to the nitrogen, the  $k$  value increases with increasing aromaticity, whereas for the other type of nitrogen solutes it is the effect of the steric accessibility of the nitrogen atom that plays the major role, as is seen on the case of the two quinoline isomers<sup>10</sup>.

It can be concluded that the silica gel with a chemically bonded amino phase, Separon SIX NH<sub>2</sub>, can serve well for the separation of aromatic hydrocarbons into groups characterized by the number of aromatic nuclei in their molecules. In this respect the packing compares well with other amino<sup>2,4</sup> and diamino<sup>5,6</sup> phases.

TABLE III  
Capacity ratios of some heterocyclic compounds

Compound	$k^a$	$s \cdot 10^3$ <sup>a</sup>
Pyridine	4.896	3.075
Indole	48.762	13.221
Benzo[ <i>b</i> ]-naphtho[2,3- <i>d</i> ]-furan	1.051	3.401
Thianthrene	0.870	2.850

<sup>a</sup> Calculated from five replicate measurements.

TABLE IV  
Capacity ratios of some nitrogen heterocyclic compounds

Compound	$k^a$	$s \cdot 10^3$ <sup>a</sup>
Pyridine	1.020	3.711
Carbazole	5.986	2.875
Indole	5.612	3.415
Benzo[ <i>c</i> ]quinoline	0.328	1.875
Benzo[ <i>f</i> ]quinoline	1.231	2.130
Dibenzo[ <i>a,j</i> ]carbazole	14.798	7.819

<sup>a</sup> Calculated from five replicate measurements.

TABLE V  
Ranges of log  $I_x$  values for groups of aromatic hydrocarbons and various amino phases

Aromatic hydrocarbons	Separon SIX NH <sub>2</sub>	Bondapak NH <sub>2</sub> <sup>a</sup>	Silica-R(NH <sub>2</sub> ) <sub>2</sub> <sup>b</sup>	Chromegabond (NH <sub>2</sub> ) <sub>2</sub> <sup>c</sup>
Mononuclear	1.00--1.50	0.50--1.00	1.00--1.22	0.55--1.35
Binuclear	1.76--2.50	1.92--2.25	1.76--2.59	1.65--2.11
Trinuclear	2.50--3.50	2.61--3.40	2.48--3.87	2.45--3.87
Tetranuclear	3.30--4.10	3.39--4.09	3.02--4.85	2.98--4.12
Pentanuclear and more	>4.11	>4.30	>5.00	>4.79

<sup>a</sup> Ref. 2; <sup>b</sup> ref. 5; <sup>c</sup> ref. 6.

The log  $I_x$  limits found in this work are compared with the available published data in Table V; here the fact that the set of standards used by us was somewhat different from that used in the papers cited has to be taken into account.

Tables II and III demonstrate that sulphur and oxygen heterocycles, which are always present in natural hydrocarbon mixtures, will elute together with the related aromatics, whereas nitrogen compounds will attain substantially higher capacity ratios.

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