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INFLUENCE OF THE MOLECULAR STRUCTURE OF AROMATIC HYDROCARBONS ON THEIR ADSORPTIVITY ON ALUMINA

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SUMMARY

The adsorption chromatography of aromatic hydrocarbons was studied for the adsorption system alumina–*n*-pentane. The importance of the planarity of the molecules, acid–base interactions of some types of hydrocarbons with the alumina surface and alkylation at different positions in polynuclear aromatics was shown. A series of standards was selected with fixed values of retention indices. The retention indices of the other aromatic hydrocarbons were calculated by means of interpolation or extrapolation, as with Kováts indices in gas chromatography.

INTRODUCTION

Adsorption elution chromatography (AEC) can be used not only as a separation technique when a mixture of compounds has to be isolated for further analysis, but also as an identification method. The use of sensitive UV detectors enables analyses of aromatic hydrocarbons to be carried out under ideal conditions, *i.e.*, in the region of the linear part of the adsorption isotherm. In this way, it is possible to employ adsorption chromatography for differentiating a series of substances, the separation of which by gas chromatography is sometimes very difficult.

For the successful use of AEC for identification purposes, it is necessary, above all, to know the adsorption properties of the solutes. These properties are very difficult to establish and although they have recently been thoroughly investigated, especially by Snyder[1-3], many problems remain unsolved, even for relatively simple substances such as aromatic hydrocarbons.

The aim of this work was to determine the influence of the molecular structure of an aromatic hydrocarbon upon its adsorptivity. The results make it possible not only to predict the possibilities for the separation of single types of aromatic hydrocarbons, but also to identify these substances.

In this work we have been concerned with the AEC of aromatic hydrocarbons on alumina with *n*-pentane as the eluent. The results are also applicable to adsorption chromatography of aromatic hydrocarbons on alumina when alkanes or isoalkanes are used as eluents.

EXPERIMENTAL

Adsorbents

Acidic, neutral and basic alumina (Woelm, Eschwege, G.F.R.) was used (surface pH values 4, 7.5 and 10, respectively). Before use, the adsorbents were calcined at 400° for 8 h, and then deactivated by the addition of water (1.5, 2.0, 3.5 and 4.5%, w/w).

Columns

Columns of lengths 50 and 100 cm and I.D. 3 mm (Nester-Faust, Newark, Del., U.S.A.) containing 2.9 and 5.75 g of adsorbent, respectively, were used. The eluent flow-rate was maintained at 60–65 ml/h. All the measurements were carried out with a low loading of the adsorption column (less than 10^{-5} g/g). A sensitive UV detector was used and good reproducibility of the results was achieved.

Detector

A differential UV detector (Waters Ass., Framingham, Mass., U.S.A.), operating at a wavelength of 254 nm, was used with a cell of optical path length of 1.0 cm and a dead volume of 8 μl.

Eluent

Only *n*-pentane was used as the eluent. Before use, it was dried and distilled. Its purity was checked by means of an SP 800 B UV spectrophotometer (Pye Unicam Ltd., Cambridge, Great Britain).

Pump

An MC 300 piston micropump (Mikrotechna, Prague, Czechoslovakia), adapted as double-acting and equipped with pulse damper was used.

Treatment of results

The measured retention values were treated by the method proposed by Snyder[3], which permits the mutual re-calculation of the measured retention volumes on aluminas with different activities. The results are expressed as so-called adsorption energies, $S°$, for which, in the system alumina–*n*-pentane, the following equation is valid:

$$\log R° = \log V_a + aS° \tag{1}$$

where V_a and a are parameters characterizing the adsorbent activity and $R°$ is the specific retention volume (ml/g).

RESULTS AND DISCUSSION

The retention volumes of parent aromatic hydrocarbons were measured and then converted into adsorption energies, $S°$, which were compared with the empirical relationship proposed by Snyder:

$$S° = 0.31 \cdot nC_a \tag{2}$$

where nC_a is a number of aromatic carbon atoms in the molecule.

It was found that eqn. 2 is suitable for hydrocarbons with 1–3 aromatic rings and a planar molecule. Aromatics with a planar molecule and more rings have a higher adsorption energy and, as the number of rings increases, an increase in the deviation from eqn. 2 towards higher values of the adsorption energy takes place, as can be seen in Fig. 1.
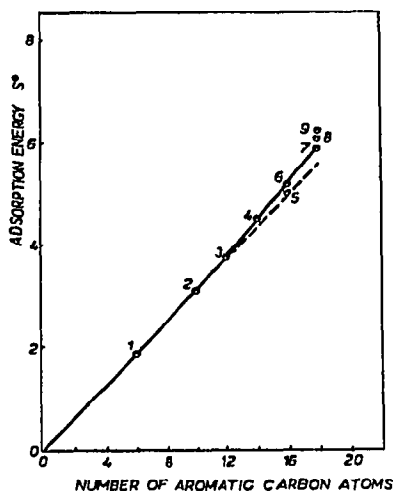

Fig. 1. Dependence of adsorption energy, $S°$, on the number of aromatic carbon atoms. Broken line, theoretical relationship according to eqn. 2; solid line, experimental relationship. 1 = Benzene; 2 = naphthalene; 3 = diphenylene; 4 = phenanthrene; 5 = pyrene; 6 = fluoranthene; 7 = triphenylene; 8 = 1,2-benzanthracene; 9 = chrysene.

Aromatic hydrocarbons with non-planar molecules (diphenyl, m- and p-terphenyl and 3,4-benzophenanthrene) show deviations towards lower adsorption energies (Table I), this effect being in good agreement with the assumption that the planarity of the molecule has a decisive influence on adsorption on alumina. At present, it is not known how to predict this deviation of the adsorption energy and only experimental values are used.

Aromatics, in the case of which, in addition to an inductive interaction between the adsorbent and the adsorbate, an acid–base interaction also takes place, give higher values of $S°$. Aromatic hydrocarbons that have an acidic hydrogen atom in the molecule (indene, fluorene and benzofluorenes) and hydrocarbons with a low ionization potential (anthracene, tetracene and pentacene) show different adsorption energies on the

TABLE I

ADSORPTION ENERGIES, $S°$, OF NON-PLANAR AROMATIC HYDROCARBONS

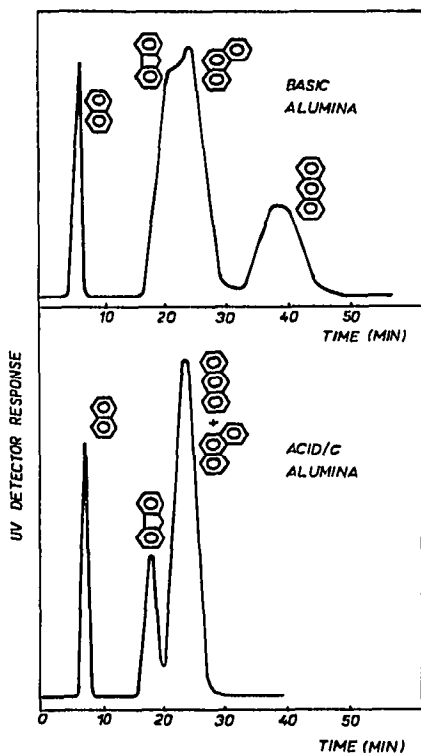| Solute	$S°_{th}$	$S°_{exp}$	$S°_{th-exp}$
Diphenyl	3.72	3.42	+0.30
m-Terphenyl	5.58	4.70	+0.88
p-Terphenyl	5.58	5.20	+0.38
3,4-Benzophenanthrene	5.58	4.90	+0.68

Fig. 2. Chromatograms of the mixture of standards on basic and acidic alumina. Column, 1 m long, I.D. 3 mm; eluent, *n*-pentane.

various aluminas, depending of the surface pH of the adsorbent used. The chromatogram of a mixture of naphthalene, fluorene, phenanthrene and anthracene on a basic and an acidic alumina (the pHs of the surfaces being 10 and 4, respectively), illustrates this effect (Fig. 2). On basic alumina, the separation of fluorene from phenanthrene was poor, while phenanthrene and anthracene were separated completely; on the acidic alumina, fluorene was well separated, and anthracene was eluted together with phenanthrene. The differences between the measured adsorption energies of fluorene and anthracene were $\Delta S^\circ = 0.11$ and 0.29, respectively.

The problems involved in the adsorption behaviour of alkylaromatics are much more complicated than they might seem at first sight. From the point of view of alkylation, single carbon atoms in the aromatic hydrocarbon, beginning with naphthalene, do not have equivalent positions, which is why the contributions of ΔS° of alkyl groups are different for different alkyl positions in a molecule of naphthalene, fluorene, phenanthrene or anthracene (Fig. 3). It was found that the contributions of ΔS° for 9-alkylanthracenes, 1-alkylnaphthalenes and alkylbenzenes are virtually the same. With 2-alkylnaphthalenes, this change is about double that of alkylbenzenes and for 2-alkylanthracenes, 2-alkylphenanthrenes and 1-alkylfluorenes, it is four times larger than for alkylbenzenes (Fig. 3).

The adsorption properties of monoalkylated aromatics substituted by different
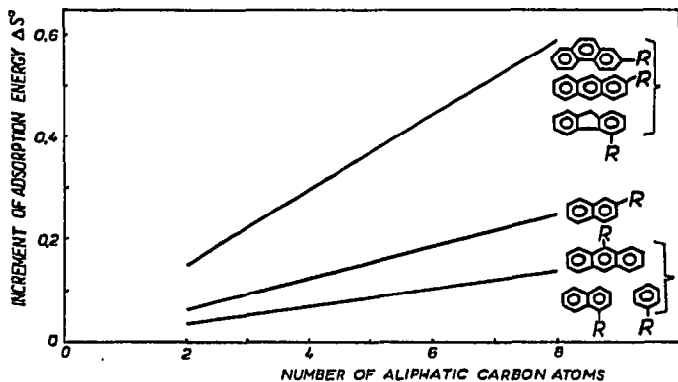
Fig. 3. Incremental adsorption energy, $\Delta S°$, for aliphatic substitution in different positions.

alkyl groups in the same position show some general regularities. With n-alkyl groups, the adsorption energy increases in a linear manner as a function of the increase in chain length up to C_8–C_{10}. An exception occurs in the case of a methyl group, for which $S°$ is always higher than the values for ethyl and propyl groups. Branching of an alkyl group on an α-carbon atom causes a decrease in the adsorption energy when the alkylated molecule is planar. This effect is greatest when free rotation about the α-carbon atom is possible and the branching of the alkyl chain is symmetrical (e.g.,
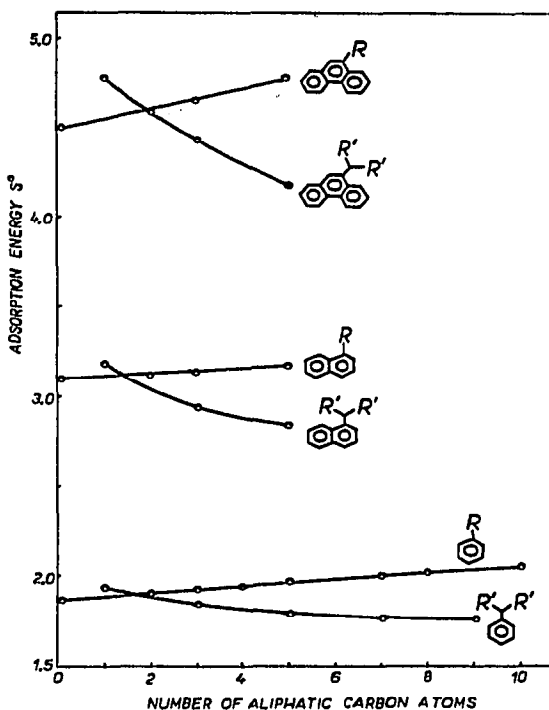

Fig. 4. Adsorption energy, $S°$, versus the number of aliphatic carbon atoms for n-alkyl aromatics and alkyl aromatics symmetrically branched on the α-carbon atom.

isopropyl or 3-amyl) (Fig. 4). The presence of a bulky rotating isoalkyl group leads to steric hindrance to adsorption, which results in a decrease in the adsorption energy.

Branching of an alkyl group situated on a β-carbon atom has an effect similar to that of branching on an α-carbon atom, but the decrease in the retention volume, in relation to that of the n-alkyl group, cannot be used for separation purposes. The adsorption energies of cycloalkyl groups and alkyl groups branched in the γ- or further positions from the aromatic ring are virtually the same as those of the corresponding n-alkyl groups[4].

Cyclanoaromatics containing 1–3 naphthenic rings in the molecule were studied in order to determine the extent to which closure of a saturated ring would affect the adsorption energy. The retention volumes of indane, tetralin, 2a,3,4,5-tetrahydroacenaphthene, 1,2,3,4,5,6,7,8-octahydroanthracene, 1,2,3,3a,4,5,5a,6,7,8-decahydropyrene and 1,2,3,4-tetrahydrophenanthrene were measured and it was found that their adsorption energies are in very good agreement with the energies of the corresponding polymethylaromatics, as shown in Table II. Further alkylation of the aromatic ring

TABLE II

ADSORPTION ENERGIES, $S°$, OF NAPHTHENIC AROMATICS AND THE CORRESPONDING POLYMETHYL AROMATICS

Solute	$S°$	Solute	$S°$
Indane	2.14	o-Xylene	2.12
Tetralin	2.16		
2a,3,4,5-Tetrahydroacenaphthene	2.36	1,2,3-Trimethylbenzene	2.28
1,2,3,4,5,6,7,8-Octahydroanthracene	2.32	1,2,4,5-Tetramethylbenzene	2.28
1,2,3,4-Tetrahydrophenanthrene	3.49	1,2-Dimethylnaphthalene	3.46
1,2,3,3a,4,5,5a,6,7,8-Decahydropyrene	2.44	1,2,3,4-Tetramethylbenzene	2.40

causes a change in $S°$ that corresponds to the alkylation of an aromatic molecule. Alkylation on the naphthenic ring does not cause any changes.

The retention volumes of diphenylalkanes illustrate the importance of the planarity of a molecule in relation to the adsorption. Diphenylalkanes (diphenylmethane, 1,2-diphenylethane, 1,4-diphenylbutane and 1,6-diphenylhexane) form a separate group with common properties. Of these substances, diphenylmethane has the lowest adsorption energy. The arrangement of its molecule does not allow the benzene rings to form a coplanar configuration with the adsorbent surface. It can be presumed that only the vector of the adsorption forces perpendicular to the surface of the adsorbent is applied. The angle of the axes of both aromatic rings is the smallest in diphenylmethane and 1,1-diphenylethane, and consequently these compounds have low adsorption energies. For further members of this series, the single bonds of the aliphatic chain allow the phenyl groups to take up more advantageous positions towards the adsorbent surface. Therefore, the adsorption energy of 1,2-diphenylethane is higher than that of diphenylmethane. When the phenyl groups are moved further along the chain, the value of $S°$ decreases slightly (Table III).

The dibenzocyclanes diphenylene, fluorene, 9,10-dihydroanthracene, 1,2:4,5-dibenzocycloheptane and 1,2:5,6-dibenzocyclooctane were studied. The first two members of this series are planar. The value of $S°$ for diphenylene agrees exactly with eqn. 2,

TABLE III

ADSORPTION ENERGIES, $S°$, OF DIPHENYLALKANES AND DIBENZOCYCLOALKANES

Solute	$S°$
Diphenylmethane	3.12
1,1-Diphenylethane	3.11
1,2-Diphenylethane	3.36
1,4-Diphenylbutane	3.32
1,6-Diphenylhexane	3.28
Diphenylene	3.74
Fluorene	4.32
9,10-Dihydroanthracene	3.94
1,2:4,5-Dibenzocycloheptane	3.68
1,2:5,6-Dibenzocyclooctane	3.58

while the adsorption energy of fluorene is much higher. The cause of this exception has already been discussed. The other dibenzocycloalkanes have non-planar molecules and, therefore, a decrease in their $S°$ values, beginning with 9,10-dihydroanthracene, takes place. This decrease continues as the distance between the two aromatic rings increases (Table III).

Our results show the complexity of this problem and the necessity for further detailed studies on the influence of the structure of aromatic hydrocarbons on their adsorptivity to be carried out. Eventually, the theoretical calculation of the retention volume of any aromatic hydrocarbon should be possible.

Retention indices of aromatic hydrocarbons

The method of calculating adsorption energies in this work is based on the assignment of a fixed value of $S°$ to certain hydrocarbons, and then the values for the other substances can be calculated from these fixed values according to eqn. 1. As shown, $S°$ is not a linear function of the number of aromatic carbon atoms, which may cause inaccuracies when choosing a standard. Even published experimental values of $S°$ sometimes differ[1-3]. When an unsuitable standard is chosen, fluorene or anthracene, for example, the measured values of the retention volume depend on the pH of the alumina surface. As is evident from the results obtained, when different types of alumina are used, very different values of $S°$ may be obtained.

On the basis of the results, we chose the following series of standards: benzene, naphthalene, phenanthrene and 1,2-benzanthracene. A retention index of $I = 10$ was assigned to the first member (benzene), 100 to naphthalene, 1000 to phenanthrene and 10,000 to 1,2-benzanthracene. A retention index of an unknown aromatic hydrocarbon is then calculated in an analogous manner to the calculation of Kováts indices, in accordance with the following equation:

$$\log I_x = \log I_n + \frac{\log R_x - \log R_n}{\log R_{n+1} - \log R_n} \tag{3}$$

where x, n, $n + 1$ represent the unknown substances and the lower and higher standards, respectively and the R values are the corresponding corrected elution volumes.

Eqn. 3 is valid for calculating retention indices, I, of substances the elution volumes of which are higher than that of benzene.

For substances with lower elution volumes, the linear dependence log R *versus* log I for the interval $10 \leqslant I \leqslant 100$ was extrapolated to the region of $I < 10$. This resulted in eqn. 4, which defines the retention indices of substances with elution volumes lower than that of benzene:

$$\log I_x = 1 - \frac{\log R_B - \log R_x}{\log R_N - \log R_B} \tag{4}$$

where R_N is the corrected elution volume of naphthalene and R_B the corrected elution volume of benzene.

In Table IV, the retention indices of 100 aromatic hydrocarbons with 6–19

TABLE IV

RETENTION INDICES, I, OF AROMATIC HYDROCARBONS

Solute	Number of carbon atoms	I
Alkylbenzenes		
Benzene	6	10
Toluene	7	11.1
Ethylbenzene	8	10.8
m-Xylene	8	12.1
o-Xylene	8	16.2
Isopropylbenzene	9	9.6
n-Propylbenzene	9	11.2
1,2,4-Trimethylbenzene	9	16.8
1,2,3-Trimethylbenzene	9	21.8
sec.-Butylbenzene	10	9.5
tert.-Butylbenzene	10	10.0
Isobutylbenzene	10	11.2
n-Butylbenzene	10	11.6
1,2,4,5-Tetramethylbenzene	10	21.8
1,2,3,4-Tetramethylbenzene	10	27.3
3-Phenylpentane	11	8.6
tert.-Amylbenzene	11	9.3
2-Phenylpentane	11	9.5
2-Phenyl-3-methylbutane	11	9.5
Neopentylbenzene	11	10.7
1-Phenyl-2-methylbutane	11	10.9
1-Phenyl-3-methylbutane	11	11.8
n-Amylbenzene	11	12.0
Cyclopentylbenzene	11	12.2
m-Diisopropylbenzene	12	8.6
Cyclohexylbenzene	12	12.3
4-Phenylheptane	13	8.3
n-Heptylbenzene	13	12.9
n-Octylbenzene	14	13.5
5-Phenylnonane	15	7.8
n-Decylbenzene	16	14.0

TABLE IV *(continued)*

Solute	Number of carbon atoms	I
Indanes, tetralins		
Indane	9	16.8
1-Methylindane	10	15.9
5-Methylindane	10	16.8
Tetralin	10	17.5
4-Methylindane	10	21.0
5-Ethylindane	11	14.8
6-Methyltetralin	11	18.8
Naphthalenes		
Naphthalene	10	100.0
1-Methylnaphthalene	11	114
2-Methylnaphthalene	11	130
1,4-Dimethylnaphthalene	12	95
1-Ethylnaphthalene	12	102
1,5-Dimethylnaphthalene	12	110
2-Ethylnaphthalene	12	124
1,7-Dimethylnaphthalene	12	150
1,3-Dimethylnaphthalene	12	153
1,2-Dimethylnaphthalene	12	180
2,7-Dimethylnaphthalene	12	200
2,3-Dimethylnaphthalene	12	210
1-Isopropylnaphthalene	13	73
1-*n*-Propylnaphthalene	13	107
1-(3-Amyl)naphthalene	15	60
1-*n*-Amylnaphthalene	15	114
1-Phenylnaphthalene	16	268
2-Phenylnaphthalene	16	1394
Diphenyls, terphenyls, diphenylalkanes		
Diphenyl	12	169
Diphenylmethane	13	103
3-Methyldiphenyl	13	153
1,1-Diphenylethane	14	102
1,2-Diphenylethane	14	153
3-Isopropyldiphenyl	15	118
1,4-Diphenylbutane	16	144
1,6-Diphenylhexane	18	135
m-Terphenyl	18	1330
p-Terphenyl	18	2740
Dibenzocycloalkanes		
Diphenylene	12	287
Fluorene	13	611; 744*
9,10-Dihydroanthracene	14	399
1,2:4,5-Dibenzocycloheptane	15	260
1,2:5,6-Dibenzocyclooctane	16	220
Phenanthrenes, anthracenes		
Phenanthrene	14	1000
Anthracene	14	1000; 1520*
9-Methylanthracene	15	1390**
9-Methylphenanthrene	15	1500
1-Methylphenanthrene	15	1520

TABLE IV *(continued)*

Solute	Number of carbon atoms	I
3-Methylphenanthrene	15	1630
2-Methylphenanthrene	15	1680
2-Methylanthracene	15	2240**
9-Ethylphenanthrene	16	1120
3,6-Dimethylphenanthrene	16	1700
9-Isopropylphenanthrene	17	910
9-*n*-Propylphenanthrene	17	1260
9-(3-Amyl)phenanthrene	19	590
9-*n*-Amylphenanthrene	19	1590
Naphthenic aromatics		
2a,3,4,5-Tetrahydroacenaphthene	12	25.3
Acenaphthene	12	200
1,2,3,4,5,6,7,8-Octahydroanthracene	14	23.5
1,2,3,4-Tetrahydrophenanthrene	14	190
1,2,3,3a,4,5,5a,6,7,8-Decahydropyrene	16	29.4
Others		
Acenaphthylene	12	286
9-Methylfluorene	14	563**
1-Methylfluorene	14	1205**
4,5-Methylenephenanthrene	15	1705
Pyrene	16	2060
Fluoranthene	16	2550
3,4-Benzophenanthrene	18	1780
Triphenylene	18	7510
1,2-Benzanthracene	18	10,000
Chrysene	18	11,600

* Retention data on acidic and basic alumina, respectively.
** Retention data on neutral alumina.

carbon atoms in their molecules are given. The retention index of chrysene for log $I > 4$ was obtained by an extrapolation analogous to that for log $I < 1$.

When eqns. 1 and 3 are combined, the following equation is obtained:

$$\log I_x = \log I_n + \frac{S_x^\circ - S_n^\circ}{S_{n+1}^\circ - S_n^\circ} \tag{5}$$

Eqn. 5 enables retention indices to be calculated from given values of S°. Eqn. 5 is valid only for substances with elution volumes higher than that of benzene. The following values of the adsorption energies of standards are used: benzene 1.86, naphthalene 3.10, phenanthrene 4.50 and 1,2-benzanthracene 6.10.

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