Journal of Chromatography, 117 (1976) 117–127
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CHROM. 8709

INFLUENCE OF THE MOLECULAR STRUCTURE OF AROMATIC HYDROCARBONS ON THEIR ADSORPTIVITY ON SILICA GEL

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(First received June 13th, 1975; revised manuscript received August 28th, 1975)

SUMMARY

The liquid–solid chromatography of aromatic hydrocarbons was studied on the system silica gel–*n*-pentane and retention indices for 113 aromatics are presented. The suggested procedure enables one to calculate the elution volumes of parent polynuclear aromatic hydrocarbons and to predict the adsorptivities of alkylaromatic hydrocarbons and naphthenoaromatic hydrocarbons. The results for diphenylalkanes, diphenylalkenes and polyphenyls and the effect of bridging methylene groups show the complexity of this problem.

INTRODUCTION

This study was an extension of previous work[1–3] on the effect of the molecular structure of aromatic hydrocarbons on their adsorptivity. Most of the previous results were obtained on alumina; alkylnaphthalenes and alkylphenanthrenes were also studied on silica gel[3]. The results indicated that in addition to alumina, silica gel can also be used with advantage for the preparation and identification of aromatic hydrocarbons, bearing in mind the specific properties and different type of adsorption process on silica gel compared with that on alumina[4].

The adsorption chromatography of aromatic hydrocarbons on silica gel and the interpretation of the retention data have received less attention than those for alumina. The detailed measurement of the retention data of various types of aromatic hydrocarbons would help to extend the presently incomplete knowledge in this area.

In this work, the retention data of 113 aromatic hydrocarbons of various structural types were measured; the results were expressed as retention indices[1], from which general conclusions about the adsorption behaviour of the various aromatic hydrocarbons were drawn.

EXPERIMENTAL

Adsorbent

Silica gel CT (Reeve Angel, London, Great Britain) was used in the form of irregular particles of average particle size 11 μm. The column was filled by the slurry packing technique with bromoform–carbon tetrachloride. The activity of the adsorbent is apparent from the values of the capacity factors, k', for selected standards (Table I).

Eluent

Distilled *n*-pentane, dried by percolation through a column of silica gel, was used as the eluent. Its purity was checked by UV spectrophotometry.

Column

A thick-walled glass column, 75 cm × 0.22 cm I.D. was used with an eluent flow-rate of 33 ml/h and an operating pressure of 30 atm.

Detector

A differential UV monitor (Waters Assoc., Milford, Mass., U.S.A.), operating at a wavelength of 254 nm with a cell of optical path length 1 cm and cell volume 8 μl was used.

Procedure

The elution volumes of solutes were measured simultaneously with the elution volumes of standards [benzene, naphthalene, phenanthrene and benzo(*a*)anthracene] and retention indices, *I*, were calculated as described previously[1], in accordance with the equation

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

where x, n and $n+1$ represent the solute and the lower and higher standards, respectively, and the R values are the corresponding corrected retention volumes (observed retention volume minus the bed free volume). The standards were assigned the following retention indices: benzene 10, naphthalene 100, phenanthrene 1000 and benzo(*a*)anthracene 10,000. In this work solutes with high retention indices ($\log I_x > 6$) were used, and it was therefore decided to add to the group of standards benzo(*b*)chrysene, which has $I = 100{,}000$, thus enabling the slight differences in adsorbent activity caused by variations in the water content of the eluent to be eliminated.

RESULTS AND DISCUSSION

Parent aromatic hydrocarbons

For parent catacondensed aromatic hydrocarbons (Table I), there is a linear dependence of log *I* on the number of aromatic carbon atoms. Condensation of another aromatic ring (four aromatic carbon atoms) on to a parent aromatic hydrocarbon is accompanied by an increment $\Delta \log I = 1.0$, and for one aromatic carbon atom the increment is $\Delta \log I = 0.25$.

It was found that the following equation is valid for the measured set of catacondensed aromatic hydrocarbons:

$$\log I = 0.25\, nC_{AR} - 0.5 \tag{2}$$

where nC_{AR} is the number of aromatic carbon atoms in the molecule.

TABLE I

RETENTION INDICES OF CATACONDENSED AROMATIC HYDROCARBONS

Hydrocarbon	*Log $I_{meas.}$*	*Log $I_{calc.}$**	*Capacity factor, k'*
Benzene	1.000	1.000	0.88
Naphthalene	2.000	2.000	1.88
Biphenylene	2.491	2.500	
Anthracene	2.954	3.000	
Phenanthrene	3.000	3.000	4.00
Tetracene	3.954	4.000	
Benzo(*a*)anthracene	4.000	4.000	8.25
Chrysene	4.000	4.000	
Triphenylene	4.041	4.000	
Dibenzo(*a,c*)anthracene	4.929	5.000	
Benzo(*b*)chrysene	5.000	5.000	17.25
Picene[benzo(*a*)chrysene]	5.068	5.000	

* Calculated according to eqn. 2.

The retention data for pericondensed aromatic hydrocarbons showed that carbon atoms that belong to three aromatic rings (so-called peri-carbon atoms) have a lower adsorptivity than the other aromatic carbon atoms. It was found that the appropriate increment for one peri-carbon atom is $\Delta \log I = 0.05$, while the increment for the remaining aromatic carbon atoms is the same as for catacondensed aromatic hydrocarbons, *i.e.*, $\Delta \log I = 0.25$ for one aromatic carbon atom (Table II).

TABLE II

RETENTION INDICES OF PERICONDENSED AROMATIC HYDROCARBONS

Hydrocarbon	*Log $I_{meas.}$*	*Log $I_{calc.}$**
Pyrene	3.061	3.100
Fluoranthene	3.423	3.300
Benzo(*a*)pyrene	4.111	4.100
Benzo(*e*)pyrene	4.176	4.100
Perylene	4.204	4.100
Benzo(*k*)fluoranthene	4.418	4.300
Benzo(*g,h,i*)perylene	4.212	4.200
Anthanthrene	4.344	4.200
o-Phenylenepyrene	4.447	4.400
Coronene	4.301	4.300
Dibenzo(*a,e*)pyrene	5.045	5.100
Dibenzo(*b,e*)pyrene	5.068	5.100
Benzo(*r,s,t*)pentaphene	5.097	5.100

* Calculated according to eqn. 3.

The retention indices of pericondensed aromatic hydrocarbons are calculated according to the following equation:

$$\log I = 0.25\, nC_{AR} - 0.2\, nC_{PE} - 0.5 \tag{3}$$

where nC_{AR} is the total number of aromatic carbon atoms and nC_{PE} is the number of peri-carbon atoms in the molecule.

The results in Tables I and II were compared with those obtained by other workers[4–7]. In all instances it was found that there were no changes in the order of elution of solutes and, where published data permitted the calculation of retention indices[4,5], good agreement was obtained. The differences in the retention indices of benzo(*a*)pyrene and benzo(*e*)pyrene are in accordance with the results published by Strubert[6]. These differences indicate that there are also steric interactions that affect the separation of isomers.

Alkylaromatic hydrocarbons

In accordance with the results reported previously[3], an increase in the retention index was found to be caused only by substitution by a methyl or ethyl group, substitution by a propyl group having virtually no effect on the retention index (Table III). On lengthening the alkyl group further, the retention index tends to decrease, by an amount proportional to the increase in the number of carbon atoms in the alkyl group. On silica gel, in contrast to alumina, substitution by an isopropyl group or higher groups branched at the α-carbon atom was found to cause no steric hindrance to adsorption, so that branching of the alkyl group has virtually no effect on the retention indices of alkylaromatic hydrocarbons. The effect of the methyl groups is additive, *i.e.*, when the number of groups increases the retention index increases proportionately. These findings can be generalized to all alkylaromatic hydrocarbons, although it cannot be excluded that with eluents of higher elution strength the effect of alkylation might be partly suppressed.

In the adsorption of alkylaromatic hydrocarbons on alumina, it was observed that the individual positions in the molecule of an aromatic hydrocarbon were not equivalent[3]. A similar effect, although to a lesser extent, was also observed on silica gel, where the methylation of naphthalene in the 2-position enhances the retention index more than that in the 1-position; similarly, differences were found between 1-methyl- and 4-methylpyrene. Unlike alumina, where the contribution of the methylation of benzene to the retention index is low, on silica gel this increment is the highest ($\Delta \log I = 0.30$) among all the substances measured. Further, the group 2-methylnaphthalene, 1-methylphenanthrene, 2-methylphenanthrene and 3-methylphenanthrene follows with a mean contribution of $\Delta \log I = 0.25$.

An increment of $\Delta \log I = 0.17$ is contributed by the methyl group in the set 1-methylnaphthalene, 9-methylphenanthrene and 1-methylpyrene. In other instances the contribution by the methyl group is $\Delta \log I = 0.10$, which is insignificant from the point of view of separation from the parent aromatic system. In connection with the non-equivalence of the positions in an aromatic hydrocarbon, it should be mentioned that in arylation of aromatic hydrocarbons by a phenyl group, the order of increments for the phenyl group is the same as that for the methyl group, *i.e.*, 9-phenylanthracene < 1-phenylnaphthalene < 2-phenylnaphthalene < biphenyl.

The measurements show that the problem of the adsorption of alkylaromatic hydrocarbons on silica gel is very complicated and, in addition, the results are affected by the activity of the gel and the eluent used. As a general indication, increments of $\Delta \log I = 0.15$ per one methyl or ethyl group and zero for a propyl group give a useful guide.

Cycloalkylaromatic hydrocarbons

In most instances, the retention indices of cycloalkylaromatic hydrocarbons correspond well with those for aromatic hydrocarbons methylated in the positions where the cyclane ring is attached (Table IV); for instance, the retention index of 1,2,3,4-tetrahydroanthracene corresponds well with that of 2,3-dimethylnaphthalene. Deviations from this rule occur when the structure of the cycloalkylaromatic hydrocarbon involves methylene bridges joining two benzene rings and these bridges are not *ortho* to each other, *e.g.*, 9,10-dihydrophenanthrene and 4,5,9,10-tetrahydropyrene. In such instances the partially hydrogenated molecule possesses a higher retention index than that of the parent non-hydrogenated aromatic hydrocarbon. When the benzene rings are joined by two aliphatic chains in the *ortho* position (9,10-

TABLE III

RETENTION INDICES OF ALKYLAROMATIC HYDROCARBONS

Hydrocarbon	*Log I*	*Δlog I for alkyl*
Toluene	1.301	0.301
o-Xylene	1.580	0.580
m-Xylene	1.431	0.431
p-Xylene	1.400	0.400
1,2,4,5-Tetramethylbenzene	1.930	0.930
Pentamethylbenzene	2.255	1.255
Hexamethylbenzene	2.505	1.505
1-Methylnaphthalene	2.170	0.170
1-Ethylnaphthalene	2.179	0.179
1-*n*-Propylnaphthalene	2.029	0.029
1-*n*-Pentylnaphthalene	1.949	−0.051
1-Isopropylnaphthalene	2.130	0.130
1-(3-Pentyl)naphthalene	2.029	0.029
2-Methylnaphthalene	2.250	0.250
2-Ethylnaphthalene	2.210	0.210
1,2-Dimethylnaphthalene	2.455	0.455
2,3-Dimethylnaphthalene	2.498	0.498
1,4-Dimethylnaphthalene	2.279	0.279
1,5-Dimethylnaphthalene	2.322	0.322
2-Methylanthracene	2.973	0.019
9-Methylanthracene	3.020	0.066
9-Methylphenanthrene	3.179	0.179
9-Ethylphenanthrene	3.170	0.170
9-*n*-Propylphenanthrene	2.991	−0.009
9-*n*-Pentylphenanthrene	2.869	−0.131
9-Isopropylphenanthrene	3.029	0.029
9-(3-Pentyl)phenanthrene	2.929	−0.071
1-Methylphenanthrene	3.260	0.260
2-Methylphenanthrene	3.255	0.255
3-Methylphenanthrene	3.240	0.240
3,6-Dimethylphenanthrene	3.422	0.422
1-Methylpyrene	3.230	0.169
4-Methylpyrene	3.124	0.063
4-Methylchrysene	4.097	0.097
2-*n*-Octyltriphenylene	3.857	−0.184
3-*n*-Hexylperylene	4.041	−0.163

TABLE IV

RETENTION INDICES OF CYCLOALKYLAROMATIC HYDROCARBONS

Hydrocarbon	*Log I*
Indane	1.602
1,2,3,4-Tetrahydronaphthalene	1.699
2a,3,4,5-Tetrahydroacenaphthene	2.000
1,2,3,4,4a,9,10,10a-Octahydrophenanthrene	1.875
1,2,3,4,5,6,7,8-Octahydrophenanthrene	2.079
1,2,3,4,5,6,7,8-Octahydroanthracene	2.021
1,2,3,3a,4,5,5a,6,7,8-Decahydropyrene	2.204
1,2,3,4,4a,4b,5,6,10b,11,12,12a-Dodecahydrochrysene	1.914
1,2,3,3a,4,5,6,7,8,9,9a,10,11,12-Tetradecahydroperylene	2.090
Acenaphthene	2.301
1,2,3,4-Tetrahydrophenanthrene	2.491
1,2,3,4-Tetrahydroanthracene	2.556
1,2,3,3a,4,5-Hexahydropyrene	2.748
1,2,3,6,7,8-Hexahydropyrene	2.857
9,10-Dihydroanthracene	2.987
1,2,4,5-Dibenzocycloheptane	2.964
1,2,5,6-Dibenzocyclooctane	2.929
9,10-Dihydrophenanthrene	3.371
4,5,9,10-Tetrahydropyrene	3.716
4.5-Methylenephenanthrene	3.064
4,5-Dihydropyrene	3.230

dihydroanthracene, 1,2,4,5-dibenzocyclopentane and 1,2,5,6-dibenzocyclooctane), the retention index remains the same as that of the non-hydrogenated aromatic hydrocarbon and decreases with increasing distance between the two rings. This phenomenon will be discussed further.

From the results, it is clear that silica gel can be utilized for the separation of the hydrogenation products of aromatic hydrocarbons. This is illustrated by Fig. 1,

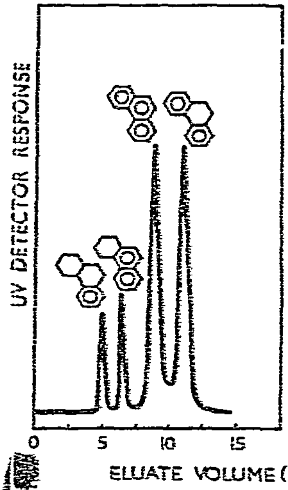

Fig. 1. Separation on silica gel of partially hydrogenated aromatic hydrocarbons obtained from hydrogenation of phenanthrene.

which shows the separation of phenanthrene and 1,2,3,4,4a,9,10,10a-octahydrophenanthrene. This separation is apparently in contradiction to other results[8].

Polyphenyls and phenyl-substituted aromatic hydrocarbons

A benzene ring attached to an aromatic hydrocarbon by a single bond increases the retention index by a value that depends on the type of hydrocarbon substituted and on the position of substitution. For silica gel, the results obtained for the alkylation of benzene are in contrast with those obtained on alumina, as mentioned in the section on alkylaromatic hydrocarbons. In accordance with this observation is phenyl substitution in the benzene molecule —the contribution of the second benzene ring in biphenyl is considerably higher than that which would correspond to six aromatic carbon atoms. The increase in the retention index accompanying the transition from biphenyl to terphenyls agrees well with the increment per one aromatic carbon atom for catacondensed aromatic hydrocarbons ($\Delta \log I = 0.265$). The planarity of the molecule has an effect, which suggests the posibility of effecting a partial separation of *o*- and *p*-terphenyl. The increment of the retention index on transition from *m*-terphenyl to *m*-quaterphenyl gives a value of $\Delta \log I = 0.245$ per one aromatic carbon atom, which again agrees very well with the value for catacondensed aromatic hydrocarbons.

The retention indices of 1- and 2-phenylnaphthalene are very different, as reported previously[4]. This can hardly be attributed to the non-planarity of the molecule of 1-phenylnaphthalene, because from the example of *o*- and *p*-terphenyl it is clear that the effect of non-planarity is low. It seems more probable to assume non-equivalence of the positions of the parent aromatic hydrocarbon, which is substituted. The study of the behaviour of alkylaromatic hydrocarbons showed that, for example, alkyl substitution of naphthalene in the 1-position always yields lower retention indices than the same alkyl substitution in the 2-position. Similarly, it was found that on silica gel, methyl substitution of anthracene in the 9-position results in a much lower increment in the retention index than methyl substitution of naphthalene in the 1- and 2-positions. In accordance with this observation it was found that phenyl substitution of anthracene in the 9- and 10-positions leads to the lowest increment in the retention index compared with other solutes measured, as shown by the results in Table V.

TABLE V

INCREMENTS IN RETENTION INDICES FOR PHENYL SUBSTITUTION

Type of substitution	*$\Delta \log I$*
Benzene → Biphenyl	1.924
Naphthalene → 2-Phenylnaphthalene	1.732
Biphenyl → *p*-Terphenyl	1.644
Biphenyl → *m*-Terphenyl	1.581
Biphenyl → *o*-Terphenyl	1.538
m-Terphenyl → *m*-Quaterphenyl	1.473
Naphthalene → 1-Phenylnaphthalene	1.415
Anthracene → 9-Phenylanthracene	1.067
9-Phenylanthracene → 9,10-Diphenylanthracene	1.109

Diphenylalkanes and related compounds

In this group of hydrocarbons, firstly the change in $\Delta \log I$ between biphenyl and diphenylmethane is very remarkable: the increment for the methyl group is 0.800, which is a higher value than the contribution of three aromatic carbon atoms. From the results in Table VI, it is obvious that further lengthening of the aliphatic chain is not accompanied by significant increments in the retention indices —the mean value per one methylene group (except the first) is $\Delta \log I = 0.12$. It can therefore be concluded that in the molecule of diphenylmethane the methyl group contributes in an extraordinary way to the adsorption on silica gel.

TABLE VI

RETENTION INDICES OF POLYPHENYLS, DIPHENYLALKANES AND RELATED COMPOUNDS

Hydrocarbon	*Log I*
Biphenyl	2.924
o-Terphenyl	4.462
m-Terphenyl	4.505
p-Terphenyl	4.568
m-Quaterphenyl	5.978
1-Phenylnaphthalene	3.415
2-Phenylnaphthalene	3.732
9-Phenylanthracene	4.021
9,10-Diphenylanthracene	5.130
Diphenylmethane	3.724
1,1-Diphenylethane	3.732
1,2-Diphenylethane	3.863
1,4-Diphenylbutane	4.176
1,6-Diphenylhexane	4.305
1,4-Dibenzylbenzene	6.002
1,2-Dibenzylbenzene	5.532
Triphenylmethane	4.929
Triptycene	5.204
cis-Stilbene	3.204
trans-Stilbene	3.633
1,4-Diphenyl-*trans,trans*-1,3-butadiene	4.328

This view is also supported by a similar difference between the retention indices of biphenylene and fluorene, where the introduction of a methylene group leads to an increment of $\Delta \log I = 0.764$. The lengthening of the alkane chain in the molecule of 9,10-dihydrophenanthrene yields an increment of $\Delta \log I = 0.116$ for the second methylene group. The effect of the methylene bridges between the two benzene rings is obvious from Fig. 2, where diphenylethane and diphenylbutane are seen to be adsorbed much more than the two stilbenes.

The substitution of the molecule of diphenylmethane by benzyl in the *para* position leads to 1,4-dibenzylbenzene. From a comparison with the retention index of *p*-terphenyl, the value of $\Delta \log I = 0.717$ for each of the methylene groups is obtained. The lower increment compared with diphenylmethane is due to the bulkier molecule, in accordance with the analogous effect observed in the group of polyphenyls. For 1,2-dibenzylbenzene, the increment of $\Delta \log I = 0.53$ per one methylene

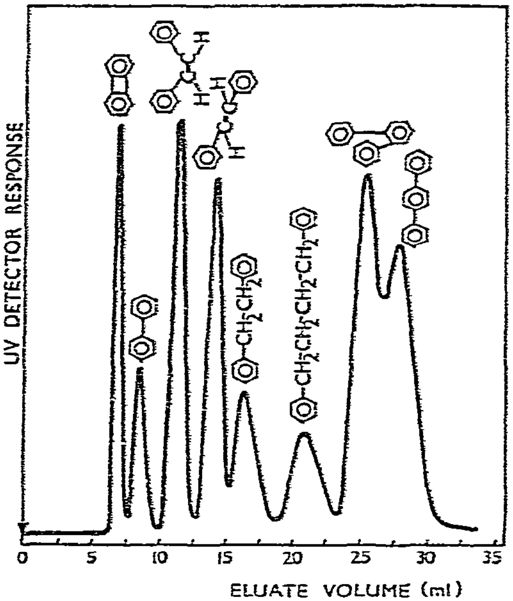

Fig. 2. Separation of diphenylalkanes, diphenylalkenes and polyphenyls on silica gel.

group follows from the comparison with *o*-terphenyl. The lower increment can be attributed to the increased non-planarity of the molecule and also to steric hindrance of the methylene groups. It seems certain that a methylene group between two aromatic rings contributes to an extraordinary extent to the adsorption of aromatic hydrocarbons on silica gel. A very strong bond is probably formed by hydrogen bridges between the methylene group and the hydroxyl groups of the silica gel. An alternative point of view was suggested by Snyder[5]. For two aromatic rings well separated by an alkyl bridge, there is an increment of localization energy which increases regularly with increasing separation of the two rings and approaches a limiting value. In dibenzocyclanes, this extraordinary property of the methylene groups does not appear. This can be explained by the substitution of the two rings in their *ortho* positions, which inhibits the resonance effect between them. In the molecule of 4,5,9,10-tetrahydropyrene, where the two ethylene bridges lie in the *meta* position, the positive effect of the methylene groups does occur, and the mean contribution for each of them is $\Delta \log I = 0.30$, which again is more than that which corresponds to an aromatic carbon atom. When the methylene group in diphenylmethane is alkylated by a methyl group to give 1,1-diphenylethane, the retention index does not change; an analogous effect occurs with the pair fluorene–9-methylfluorene. If diphenylmethane is arylated to triphenylmethane, the retention index increases by $\Delta \log I = 1.2$. This implies that the value of the adsorption energy of the methine group in triphenylmethane decreases to 65% of the adsorption energy of the methylene group in diphenylmethane.

The situation with triptycene, which has a high adsorption energy value on silica gel, is very interesting[8]. If triphenylmethane is taken as reference, the increment for the second methine group, $\Delta \log I = 0.275$, or the mean contribution per each methine group, $\Delta \log I = 0.318$, is obtained from the calculation. In the molecule of triptycene, the capacity of the methine group to form hydrogen bonds is much greater than that of the methylene groups in 9,10-dihydroanthracene, as the favourable steric arrangement of the triptycene molecule permits a resonance effect to occur. From some of the results in Tables VI and VII it can be concluded that olefinic carbons between two aromatic systems contribute only slightly to the increase in the retention index (stilbenes, dibenzocyclooctatetraene), whereas outside the aromatic system the olefinic carbons contribute to the same extent as aromatic carbons (acenaphthylene). However, this conclusion is based mainly on the comparison of the results for diphenylalkanes and diphenylpolyolefins. In this instance, the flexibility of the linkage between two rings also probably has an effect, which is greater for an alkyl than a polyvinyl linkage.

TABLE VII

RETENTION INDICES OF MISCELLANEOUS HYDROCARBONS

Hydrocarbon	*Log I*
Indene	1.813
Acenaphthylene	2.591
Fluorene	3.255
1-Methylfluorene	3.462
9-Methylfluorene	3.255
Benzo(*a*)fluorene	3.949
Benzo(*b*)fluorene	4.137
1,2,5,6-Dibenzocyclooctatetraene	2.903
3-Methylcholanthrene	4.748
5-*n*-Pentadecylacenaphthene	1.763

For this group of compounds, silica gel gives better separations than alumina. While for aromatic and alkylaromatic hydrocarbons the orders of the eluted components on silica gel and on alumina differ only very slightly, with this group of compounds considerable differences were found. For example, the separation of biphenyl, 1,2-diphenylethane adn 1,4-diphenylbutane (Fig. 2), which failed when alumina was applied, was successful on silica gel[1]. The elution order for a series of compounds is inverted, *e.g.*, for the pairs 9,10-dihydroanthracene–diphenylmethane and biphenylene–biphenyl, which indicates potentialities for both separation and identification purposes.

CONCLUSION

The results showed that the problem of measuring the elution data of aromatic hydrocarbons on silica gel is very complex. From the known elution volumes of standards, the elution volumes of fundamental catacondensed and pericondensed aromatic hydrocarbons can be calculated reliably and those of alkylaromatic hydrocarbons can be estimated approximately. Compounds that contain paraffinic or olefinic chains between two aromatic systems display deviations from the preceding group, but the results enable the retention indices to be predicted.

In comparison with alumina of the same activity, the differences between the elution volumes of the various aromatic hydrocarbons on silica gel are found to be lower and, in addition, the different adsorption of catacondensed and pericondensed aromatic hydrocarbons makes the separation of real mixtures rather complicated. On the other hand, the efficiency of columns filled with fine-mesh silica gel can be very high, and by means of the sensitive detection of the components eluted good results can be achieved during analyses of mixtures of aromatic hydrocarbons.

It must be emphasized that the results reported are valid only for the system of silica gel and a paraffinic or isoparaffinic eluent, and that changes in the order of the eluted components can occur when a more polar eluent is used.

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