ADSORPTION CHROMATOGRAPHY OF ALKYLDIAROMATICS AND ALKYLTRIAROMATICS

M.POPL, V.DOLANSKÝ and J.MOSTECKÝ

Department of Petroleum Technology and Petrochemistry,
Institute of Chemical Technology, 166 28 Prague 6

The effects of the size and the shape of the alkyl in alkylnaphthalenes and alkylphenanthrenes during adsorption elution chromatography on alumina and silica gel was investigated. From the measured retention data adsorption energies of alkylaromatics were calculated and compared with the theoretically computed values. From the results it follows that the effect of the alkyl in the molecule of aromatic compounds is quite different on alumina and on silica gel. Simultaneously differing behaviour of branched alkylaromatics was observed when compared with corresponding n-alkylaromatics on both adsorbents. An important effect on the adsorption properties of alkylaromatics is exerted by the position and the number of alkyls in the molecule.

The effect of alkyl substituents, *i.e.* their size and structure on the adsorption properties of aromatic hydrocarbons has not yet been investigated in detail (with the exception of papers[1,2]). When adsorption chromatography is used for the separation of complex mixtures of aromatic compounds[3] it is indispensable to know the adsorption behaviour of aromatics substituted by various alkyls and thus to estimate the possibilities of their mutual interference. Generally, it is known that in the case of adsorption chromatography of monosubstituted aromatics on alumina the specific retention volume increases with the length of the alkyl chain[4] and in the case of alkylbenzenes (on alumina) a certain regularity of the effect of the length and the structure of the alkyl on the retention volume of aromatics[2] has been demonstrated.

This paper is a thematic continuation of the study of elution adsorption chromatography of alkylbenzenes[2]. The aim of this study is the extension of the findings of the mentioned study on alkylnaphthalenes and alkylphenanthrenes. Simultaneously silica gel was chosen in addition to alumina as a second adsorbent. In addition to the investigation of the effect of the length and the structure of the alkyls, the effect of the position of the alkyl, and of their number and their mutual positions on the adsorption properties of aromatic hydrocarbons was also studied.

EXPERIMENTAL

The measured retention volumes were transformed to the so-called adsorption energies $S°$ according to a procedure proposed by Snyder[5]. The adsorbents used were tested with substances the $S°$ values of which are known (Table I). From the parameters thus obtained, *i.e.* α and $\log V_a$ the

adsorption energy values S_m^o were calculated which were compared with the theoretical values S_{th}^o computed on the basis of published data[5] (Table II); the results are presented as $\delta_S = S_m^o - S_{th}^o$.

RESULTS AND DISCUSSION

For the study of the effect of alkyls on the adsorption properties of aromatics alumina and silica gel were chosen as the commonest adsorbents. In all instances the measurements were carried out at a column load of 10^{-6} g/g and therefore the dependence of the retention volumes on the sample amount can be excluded. The results obtained by measurements on alumina and silica gel show that the effect of the alkyl on the two adsorbents used is manifested in quite a different manner. The majority of the measured data is in good agreement with theoretical data, as will be shown in detail later.

Retention Data Obtained on Alumina

General regularities of the effect of the size and the structure of alkyl on the retention volumes of monoalkylnaphthalenes (Table III) and monoalkylphenanthrenes (Table IV) are not too surprising in view of the earlier acquired knowledge on the behaviour of alkylbenzenes[2]. In the series of n-alkyl derivatives the equivalent retention volume increases with the increasing length of the alkyl. In the series of isoalkyls branched symmetrically on the α-carbon (with respect to the aromatic

TABLE I

Parameters of Adsorbents

Adsorbent	Water wt. %	α	$\log V_a$	Compounds used for standardization	S^o
Alumina	2·0	0·961	−1·880	benzene	1·86
				naphthalene	3·10
Alumina	3·5	0·680	−1·830	naphthalene	3·10
				phenanthrene	4·50
Silica gel	2·0	0·458	−0·042	benzene	1·5
				naphthalene	2·5
				phenanthrene	3·5
Silica gel	3·5	0·406	−0·047	benzene	1·5
				naphthalene	2·5
				phenanthrene	3·5

ring) the retention volume decreases with the alkyl size. The branching of the alkyl on the α-carbon represents an appreciable sterical hindrance of planar adsorption on alumina surface.

In both groups the greatest retention volumes were observed in pentyl and methyl derivatives. The effect of the alkyl length is more pronounced in phenanthrenes. It

TABLE II

$S°$ Values of Aromatic Hydrocarbons and Contributions of $S°$ for Alkyl Groups

Solute	Alumina		Silica gel	
	$S°$	$\Delta S°$	$S°$	$\Delta S°$
Benzene	1·86	—	1·50	—
Naphthalene	3·10	—	2·50	—
Phenanthrene	4·50	—	3·50	—
Methyl	—	+0·06	—	+0·11
Ethyl	—	+0·04	—	+0·08
n-Propyl	—	+0·06	—	+0·03
n-Pentyl	—	+0·10	—	−0·07
Isopropyl	—	−0·07	—	+0·15
3-(n-Pentyl)	—	−0·03	—	+0·05
Effect of *ortho* substitution	—	+0·09	—	—

TABLE III

Retention Data of Monoalkylnaphthalenes on Alumina and Silica Gel

Solute	Alumina, 2% wt. H_2O			Silica gel, 2% wt. H_2O		
	$R°$ ml/g	$S_m°$	δ_s	$R°$ ml/g	$S_m°$	δ_s
Naphthalene	12·59	3·10	0·00	12·43	2·48	−0·02
1-Methylnaphthalene	15·04	3·18	+0·02	15·21	2·67	+0·06
1-Ethylnaphthalene	12·97	3·11	−0·03	14·89	2·68	+0·10
1-n-Propylnaphthalene	13·80	3·14	−0·02	13·07	2·53	0·00
1-n-Pentylnaphthalene	14·95	3·18	−0·02	12·06	2·45	+0·02
1-Isopropylnaphthalene	8·70	2·93	−0·10	14·49	2·63	−0·02
1-(3-Pentyl)naphthalene	6·92	2·83	−0·24	13·03	2·53	−0·02
2-Methylnaphthalene	17·83	3·26	+0·10	16·53	2·75	+0·14
2-Ethylnaphthalene	16·77	3·23	+0·09	15·73	2·71	+0·13

was further observed that the contribution of adsorption energy for the methyl group $\Delta S^\circ = 0.06$ cannot be generalized; on the contrary this contribution should be considered as specific for each type of aromatic hydrocarbon and for each position of the alkyl. In the paper by Snyder and Buell[4] the generalization is mentioned

TABLE IV
Retention Data of Alkylphenanthrenes on Alumina and Silica Gel

Solute	Alumina, 3.5% wt. H_2O			Silica gel, 3.5% wt. H_2O		
	R° ml/g	S_m°	δ_s	R° ml/g	S_m°	δ_s
Phenanthrene	15.7	4.50	0.00	24.4	3.53	+0.03
9-Methylphenanthrene	26.5	4.78	+0.22	28.0	3.68	+0.07
9-Ethylphenanthrene	19.4	4.58	+0.04	27.7	3.67	+0.09
9-n-Propylphenanthrene	21.7	4.66	+0.10	23.5	3.49	−0.04
9-n-Pentylphenanthrene	28.1	4.82	+0.22	21.0	3.37	−0.06
9-Isopropylphenanthrene	15.4	4.44	+0.01	24.3	3.53	−0.12
9-(3-Pentyl)phenanthrene	10.3	4.18	−0.29	22.1	3.43	−0.12
1-Methylphenanthrene	26.6	4.79	+0.23	30.3	3.76	+0.15
2-Methylphenanthrene	29.6	4.86	+0.30	30.1	3.76	+0.15
3-Methylphenanthrene	28.8	4.84	+0.28	29.7	3.74	+0.13

TABLE V
Selfpolarizability Values $\pi_{\mu\mu}$ of Carbon Atoms in Aromatic Molecule and Measured Values of ΔS_m° for Methyl Group

Solute	Position	S_m°	$\pi_{\mu\mu}$ (ref.[6])
Benzene	1	0.057	0.398
Naphthalene	1	0.08	0.443
Naphthalene	2	0.16	0.405
Phenanthrene	1	0.29	0.439
Phenanthrene	2	0.36	0.403
Phenanthrene	3	0.34	0.407
Phenanthrene	9	0.28	0.442
Anthracene	2	0.40	0.411
Anthracene	9	0.07	0.526

Dimethylnaphthalene	Alumina, 2% wt. H_2O			Silica gel, 2% wt. H_2O		
	$R°$ ml/g	$S_m°$	δ_s	$R°$ ml/g	$S_m°$	δ_s
1,2-	27·53	3·46	+0·10	21·86	3·02	+0·30
1,4-	11·55	3·06	−0·16	17·30	2·80	+0·08
1,5-	14·07	3·15	−0·17	20·19	2·94	+0·22
1,7-	21·96	3·35	+0·13	20·50	2·96	+0·24
2,3-	34·78	3·56	+0·25	20·85	2·97	+0·25
2,7-	32·67	3·53	+0·31	18·91	2·88	+0·16

according to which $\Delta S°$ for alkyl increases with the number of aromatic rings in the molecule. However this applies only very approximately, because, as shown by Table V, there exist substantial exceptions to this rule. The contribution $\Delta S°$ for methyl in the case of 9-methylanthracene is practically on the same level as that of the contribution for the methyl in toluene. The difference between 1-methyl- and 2-methylnaphthalene is also considerable. Different values of $\Delta S°$ for methyl derivatives substituted in various positions of the aromatic molecule depend on the different polarizability of single carbon atoms in the aromatic molecule[6]. As seen from Table V the contribution of adsorption energy $\Delta S°$ for a corresponding methyl group decreases with the increasing polarizability of the carbon atom in the aromatic molecule, on which the methyl group is located. This is true only for single types of aromatic hydrocarbons and a comparison of various types with one another is impossible, as follows from Table V. On the basis of data given in Table VI it would be possible to determine approximately the behaviour of remaining methyl derivatives, *i.e.* 4-methylphenanthrene and 1-methylanthracene.

The presence of the second alkyl in the naphthalene molecule is another example of the deviations of the theory from experimental data. Table VI gives a series of retention data for various dimethylnaphthalenes. In general it may be said that the effect of the second methyl is considerable and in the majority of cases higher than would correspond to a double of the $\Delta S°$ contribution for methyl from Table II. Exceptions are 1,4- and 1,5-dimethylnaphthalenes for which retention volumes were measured which were lower than would correspond to theory. If experimentally measured values of $\Delta S°$ for 1-methylnaphthalene and 2-methylnaphthalene from Table V are used for the calculation of adsorption energies of dimethylnaphthalenes,

the mean deviation of δ_S decreases from 0·18 (Table VI) to 0·09. The determined differences of retention volumes are very important, as demonstrated in Fig. 1 where an example of separation of three dimethylnaphthalenes is given. A complete separation of 1,4-, 1,7-, and 2,7-dimethylnaphthalenes was achieved. These results differ from those obtained by Klemm and coworkers[1] who determined for these three isomers the same R_F values in the system alumina–cyclohexane. On the other hand a certain agreement with the data published by Kucharczyk and coworkers[7] has been achieved.

Retention Data Obtained on Silica Gel

From the results shown in Tables III and IV a good agreement of the majority of the measured data with theoretical calculations is evident, especially in the case of 1-alkylnaphthalenes and 9-alkylphenanthrenes. For naphthalenes substituted in the position 2 and for dimethylnaphthalenes the δ_S values are already substantially higher. Generally it may be stated that the effect of the alkyl group on the adsorption properties of alkylaromatics on silica gel is completely different in comparison with alumina. With an increasing number of carbon atoms in the alkyl group, from the methyl group up, the S_m^0 values decrease slowly both in n-alkyl and in isoalkylaromatics. In addition to this difference the finding is interesting that isoalkylaromatics have somewhat higher retention volumes than corresponding n-alkyl derivatives, *i.e.* that no steric hindrance is at work as in the case of adsorption on alumina.

The explanation of the differing behaviour of alkylaromatics on silica gel and alumina may be found in the character of the adsorbents themselves, *i.e.* in the type of the adsorbent–adsorbate interaction. Adsorption of a sample molecule on the surface of alumina is predominantly of an electrostatic character where the planarity of the molecule also plays a decisive role. The character of the silica gel surface is the cause of a different type of adsorption interaction. The adsorbate molecules function here as electron donors and they are bound by hydrogen bridges with the reactive and free hydroxyl groups of the adsorbent[5]. The differences of the retention
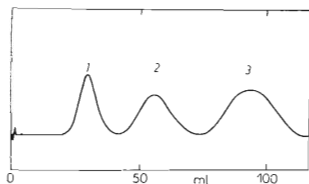
FIG. 1

Separation of Dimethylnaphthalenes on Alumina

2% wt. H_2O, n-Pentane eluent, column length 0·5 m, 3 mm I. D. *1* 1,4-Dimethyl-naphthalene; *2* 1,7-dimethylnaphthalene; *3* 2,7-dimethylnaphthalene.

volumes of alkylaromatics on silica gel may be considered as a consequence of sterical hindrance of the formation of hydrogen bonds by alkyls.

CONCLUSION

The results presented in this paper prove the appreciable reliability of the theoretical calculations used to obtain a true idea of the process of adsorption elution chromatography. However, simultaneously significant deviations from this theory were observed which complete the present knowledge on the effect of alkyl groups on the retention volumes of aromatics. It was found that the position of the alkyl in the molecule must be taken into consideration, because in some instances (naphthalene, anthracene) the differences in retention volumes of alkyl derivatives with alkyls in various positions are very substantial. In dimethylnaphthalenes it was observed that the presence of the second alkyl in the molecule usually has a stronger effect than would correspond to the sum of the contributions of both alkyls. However, even in these cases the position of the alkyls in the molecule plays its role. The effect of the alkyl differs substantially in the case of adsorption on alumina or on silica gel. On alumina n-alkyl and iso-alkylaromatics are distinctly differentiated, while on silica gel the differences in retention volumes are very small, but the retention volume of the hydrocarbon decreases in all instances with an increasing alkyl group.

REFERENCES

1. Klemm L. H., Chia D. S. W., Klopfenstein C. E., Desai K. B.: J. Chromatog. *30*, 476 (1967).
2. Popl M., Mostecký J., Dolanský V., Kuraš M.: Anal. Chem. *43*, 518 (1971).
3. Popl M., Mostecký J., Havel Z.: J. Chromatog. *53*, 233 (1970).
4. Snyder L. R., Buell B. E.: J. Chem. Eng. Data *11*, 545 (1966).
5. Snyder L. R.: *Principles of Adsorption Chromatography.* Dekker, New York 1968.
6. Streitwiesser A. jr, Brauman J. I.: *Supplemental Tables of Molecular Orbital Calculations*, Vol. 1.
7. Kucharczyk N., Fohl J., Vymětal J.: J. Chromatog. *11*, 55 (1963).

Translated by Ž. Procházka.