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HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY OF ALKYLBENZENES ON SILICA

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SUMMARY

Retention data of C_6–C_{16} alkylbenzenes, expressed in the form of capacity factor (k') and logarithms of the retention index (I) were measured on silica. The water content in the recycling mobile phase was controlled. The dependence of log I on the number of carbon atoms in the alkylbenzene molecule are given for different alkyl groups. The length of the alkyl groups, their arrangements (the *ortho*-effect) and numbers and shapes are the main factors affecting the retention of alkylbenzenes.

INTRODUCTION

The higher column efficiencies recently achieved in liquid chromatography allow a better separation of compounds separable previously only as a group.

Liquid chromatography of alkylbenzenes has been realized mostly on alumina[1–3]. The behaviour of some alkylbenzenes has been studied in gel permeation chromatography[4], and a study of the influence of the molecular structure of aromatic hydrocarbons on silica included seven alkylbenzenes[5]. Another study covered the behaviour of alkylbenzenes containing one alkyl group of various lengths (ranging from toluene to amylbenzene, and including also all polymethylbenzenes) on silica with *n*-hexane as the mobile phase[6]. The high-performance liquid chromatography (HPLC) separation of C_1–C_4 alkylbenzenes on three different reversed phases has been compared[7].

The use of preparative HPLC of alkylbenzenes leads to a more detailed separation of these compounds, which may be useful also in the case of some natural mixtures containing alkylbenzenes. When performing preparative separations of C_9 and C_{10} monoaromatic hydrocarbon mixtures on silica gel[8], it was found that the separation takes place according to: (i) the number of substituents; (ii) molecular mass; (iii) the type of hydrocarbon and (iv) the position of substituents in isomers. These criteria have also been verified for the HPLC separation of monoaromatic hydrocarbons in light and middle petroleum fractions (containing C_{10}–C_{17} hydrocarbons)[9]. The fraction of the material obtained by preparative HPLC has now been further analysed by mass spectrometry (MS), nuclear magnetic resonance (NMR) spectroscopy and analytical HPLC. The aim of the present study was to achieve a more detailed understanding of the separation mechanism.

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EXPERIMENTAL

Apparatus

A Varian 8500 liquid chromatograph (Varian, Palo Alto, CA, U.S.A.) with a syringe pump was used. Sample injection was performed by the stop flow technique with a 1-μl syringe (Hamilton, Bonaduz, Switzerland) directly into the column, using a septumless injector. A fixed-wavelength (254 nm) UV detector was employed and the chromatograph was operated at ambient temperature. Retention times were measured and printed by a CDS 111 chromatographic data system and recorded simultaneously on a dual-pen strip chart recorder (all Varian).

A stainless-steel (25 cm × 8 mm I.D.) column with tapered inlet (Varian) was filled using the slurry-packing technique with 7.5-μm irregularly shaped silica gel (Silasorb; Lachema, Brno, Czechoslovakia).

Chemicals

A series of alkylbenzene isomers was used. Some of the standards were prepared at the Prague Institute of Chemical Technology (Laboratory of Synthetic Fuels and Department of Petroleum Technology and Petrochemistry), others were commercial products from various manufacturers.

Mobile phase

n-Pentane (analytical grade) was used as the mobile phase. Before use, it was distilled in glass and dried by percolating over a silica gel column (Mikrosil, 100–150 μm; Lachema) which had been dried for 4 h at 200°C. The flow-rate of the mobile phase was 100 ml/h.

Procedure

Two or three injections were carried out for each sample, always together with a test mixture of benzene and naphthalene. As the retention differences between individual alkylbenzenes are rather small, it was necessary to maintain as stable conditions as possible in the course of measurements. Thus, closed-circuit mobile phase recycling was used, in order to eliminate the contact between the mobile phase and air moisture. A column of activated silica gel was incorporated in the circuit (Mikrosil, 80–100 μm; Lachema)[10]. Under these conditions (highly activated silica gel and dry pentane), temperature control of the system was not necessary, contrary to the procedure described in ref. 10.

Retention data are expressed in the form of the logarithm of the retention index x and capacity factor k'. The retention index system was proposed previously for liquid chromatographic retention data of aromatic hydrocarbons in adsorption systems. A retention index of $x = 10$ is assigned to benzene, 100 to naphthalene and 1000 to phenanthrene.

Retention indices for all aromatic hydrocarbons are calculated in accordance with

$$\log x = \log I_n + \frac{\log t_x - \log t_n}{\log t_{n-1} - \log t_n} \qquad (1)$$

where x, n, $n + 1$ represent the measured substance and lower and higher standards, respectively, and the t values are the corresponding adjusted retention times. Eqn. 1 is valid for substances having retention times higher than that of benzene.

For substances with lower retention times, the linear dependence of log t *versus* log I in the interval $10 \leqslant I \leqslant 100$ was extrapolated to the region of $I < 10$. This resulted in

$$\log I = 1 - \frac{\log t_B - \log t_x}{\log t_N - \log t_B} \qquad (2)$$

where t_N is the adjusted retention time of naphthalene and t_B the adjusted retention time of benzene.

Capacity factors, k', were calculated using the well-known procedure

$$k' = (t_R - t_0)/t_0$$

where t_R = retention time of the given compound and t_0 = retention time of a compound which is not adsorbed. The values of t_R were obtained by means of a back calculation from log I for the mean value of the retention time of benzene and naphthalene.

RESULTS AND DISCUSSION

The logarithms of the retention indices x and capacity factors k' are given in Table I.

Fig. 1 shows the dependence of log I on the number of carbon atoms in the alkylbenzene molecule. With increasing number of carbon atoms the range of retention data broadens. While maximum retention is limited by the straight line corresponding to the dependence for polymethylbenzenes, with every new methyl group being in the *ortho*-position (curve 1), the lower limit is formed by curve 2, which corresponds to the dependence for alkylbenzenes with the alkyl group extended in a linear manner. The minimum value on this curve corresponds to an alkylbenzene molecule with a sufficiently long alkyl chain. The two curves define the region A for most alkylbenzenes. Some alkylbenzenes have log I values which lie below curve 2 (region B), *e.g.*, compounds with two long alkyl groups (not in *ortho*-position) or with rather long branched alkyl chains.

The main factors affecting the adsorption of alkylbenzenes are as follows:

(i) the length of the alkyl group
(ii) the arrangement of the alkyl groups (the *ortho*-effect)
(iii) the number and shape of the alkyl groups

Alkyl length

Generally, alkylbenzene retention times decrease with increasing alkyl chain length. Fig. 2 demonstrates the dependence of log I on the number of carbon atoms in the molecule. As in the *n*-alkylbenzene series, a decrease in log I can be observed for the following pairs: *o*-xylene–*o*-ethyltoluene; *m*-xylene–*m*-ethyltoluene; *p*-cymene–*p*-isopropylethylbenzene; *p*-*tert.*-butyltoluene–1-ethyl-4-*tert.*-butylbenzene. Fig. 3

TABLE I

RETENTION DATA

t_R = Retention time (min); k' = capacity factor; I = retention index; $t_x = t_R - t_0$ = adjusted retention time (min).

Compound	t_x	k'	*log I*	*Δlog I*
Benzene	6.90	0.57	1	–
Naphthalene	9.13	1.08	2	–
Toluene	6.93	0.58	1.016	0.016
Ethylbenzene	6.71	0.53	0.901	−0.099
n-Propylbenzene	6.59	0.50	0.838	−0.162
n-Butylbenzene	6.46	0.47	0.764	−0.236
n-Amylbenzene	6.37	0.45	0.712	−0.288
n-Hexylbenzene	6.24	0.42	0.639	−0.361
n-Heptylbenzene	6.18	0.41	0.608	−0.392
n-Octylbenzene	6.14	0.40	0.581	−0.419
n-Decylbenzene	5.98	0.36	0.490	−0.510
o-Xylene	7.33	0.67	1.217	0.217
m-Xylene	6.91	0.57	1.005	0.005
p-Xylene	6.96	0.59	1.031	0.031
1,2,3-Trimethylbenzene	7.58	0.73	1.335	0.335
1,2,4-Trimethylbenzene	7.39	0.68	1.246	
1,3,5-Trimethylbenzene	6.92	0.58	1.009	0.009
o-Ethyltoluene	7.18	0.64	1.144	
m-Ethyltoluene	6.76	0.54	0.928	
Cumene	6.77	0.54	0.932	
1,2,3,4-Tetramethylbenzene	7.87	0.79	1.470	0.470
Isodurene	7.59	0.73	1.339	
Durene	7.51	0.71	1.301	
p-Cymene	7.07	0.61	1.089	
Isobutylbenzene	6.32	0.44	0.688	
tert.-Butylbenzene	6.72	0.53	0.906	
Pentamethylbenzene	8.11	0.85	1.575	0.575
1-Ethyl-2,4,6-trimethylbenzene	7.20	0.64	1.152	
1-Ethyl-4-isopropylbenzene	6.93	0.58	1.017	
p-*tert.*-Butyltoluene	6.56	0.49	0.818	
2-Methyl-3-phenylbutane	7.12	0.62	1.113	
Isopentylbenzene	6.26	0.43	0.655	
Neopentylbenzene	6.28	0.43	0.662	
Cyclopentylbenzene	6.89	0.57	0.994	
Hexamethylbenzene	8.64	0.97	1.803	0.803
1-Propyl-2,4,6-trimethylbenzene	6.87	0.56	0.984	
1,3,5-Triethylbenzene	6.29	0.43	0.670	
m-Diisopropylbenzene	6.35	0.45	0.705	
p-Diisopropylbenzene	6.19	0.41	0.610	
1-Ethyl-4-*tert.*-butylbenzene	6.43	0.46	0.747	
1-Propyl-2,4,6-triethylbenzene	6.22	0.42	0.631	

shows the separation of an *n*-alkylbenzene mixture. If more than one alkyl chain is extended simultaneously in a molecule, the decrease in the value of the logarithmic retention index is more pronounced, *e.g.*, mesitylene–1,3,5-triethylbenzene; *p*-xylene–*p*-diisopropylbenzene; *m*-xylene–*m*-diisopropylbenzene; 1-propyl-2,4,6-trimethylbenzene–1-propyl-2,4,6-triethylbenzene (Fig. 4). A still greater decrease in the log reten-

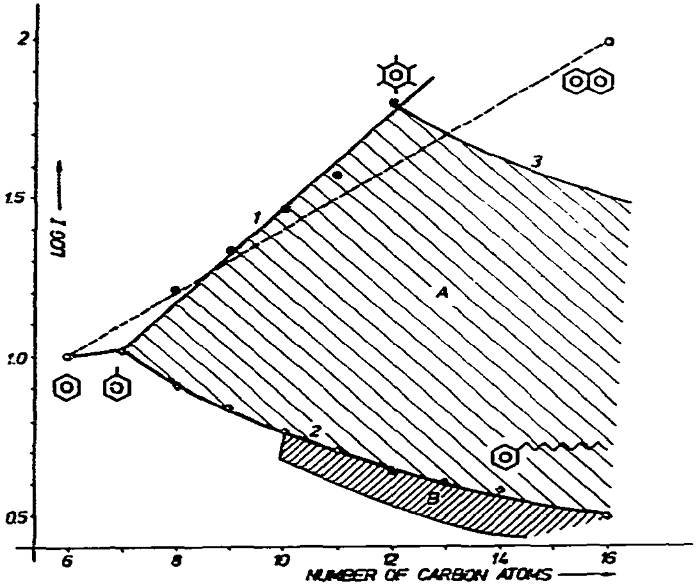

Fig. 1. Dependence of log I of alkylbenzenes on number of carbon atoms. The dashed line represents data for unsubstituted aromatic hydrocarbons, *i.e.*, benzene, naphthalene and phenanthrene.

tion index value is observed on extending an alkyl chain placed between two *ortho*-substituted methyl groups (Fig. 5, curve A).

The largest decrease in log I is observed when *tert.*-butyl replaces isopropyl (*e.g.*, *p*-cymene to *tert.*-butyltoluene, curve B) or isobutyl replaces isopropyl (*e.g.*, cumene to isobutylbenzene, curve C). Further extension of the chain to isoamyl is accompanied by a decrease in the retention index corresponding to the relevant decrease in the basic *n*-alkyl series.

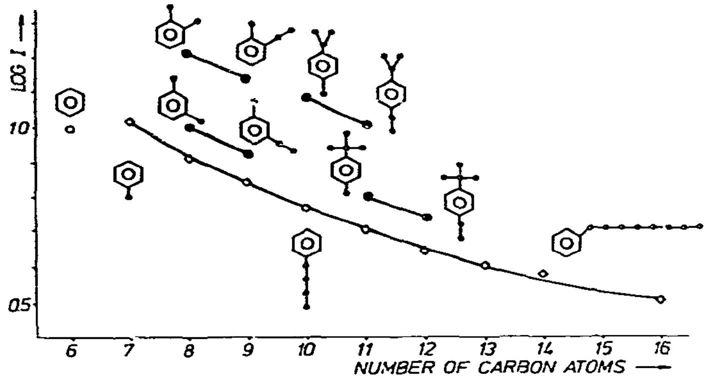

Fig. 2. Dependence of log I on number of carbon atoms for alkylbenzenes with *n*-alkyl chains.

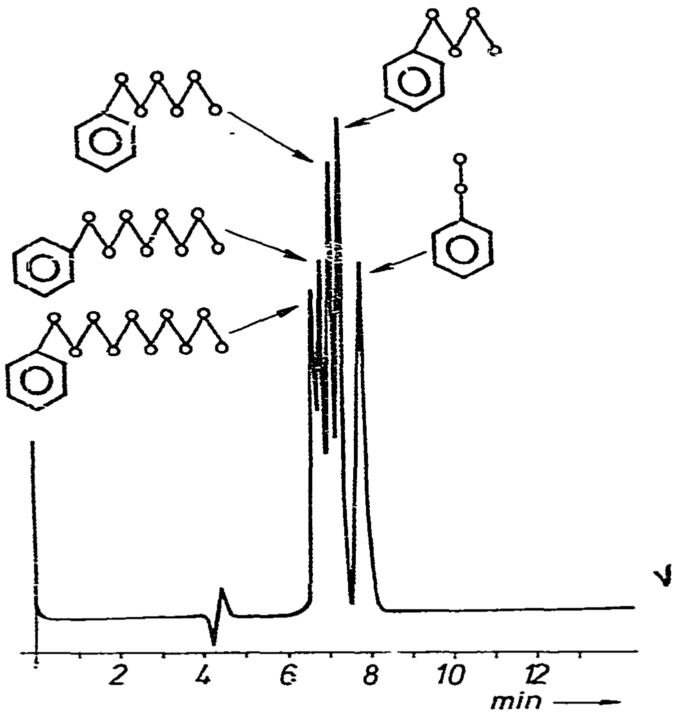

Fig. 3. Chromatogram of some *n*-alkylbenzenes. Column: 25 cm × 8 mm I.D., filled with 7.5-μm silica gel. Mobile phase: moisture controlled *n*-pentane; flow-rate 100 ml/h.

Alkyl arrangement (ortho-effect)

Generally, polymethylbenzenes have the same or longer retention times than benzene. In accordance with previous results[6,8,9], the largest increase in retention time has been found for *ortho*-substituted derivatives (Fig. 1), particularly for the so-called double *ortho*-substitution, *e.g.*, *m*-xylene and 1,3,5-trimethylbenzene or mesitylene and isodurene.

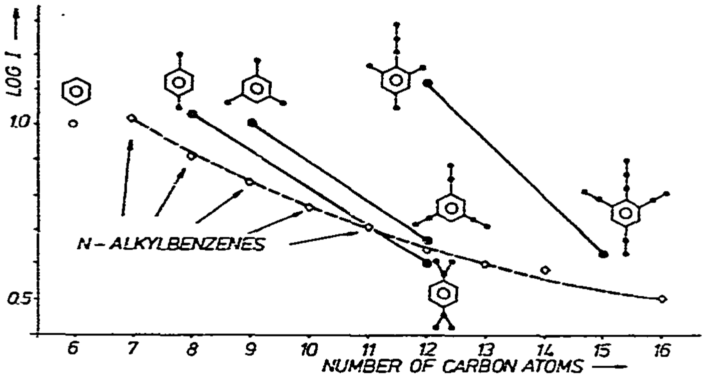

Fig. 4. Dependence of log *I* on number of carbon atoms for alkylbenzenes with extension of more than one alkyl group.

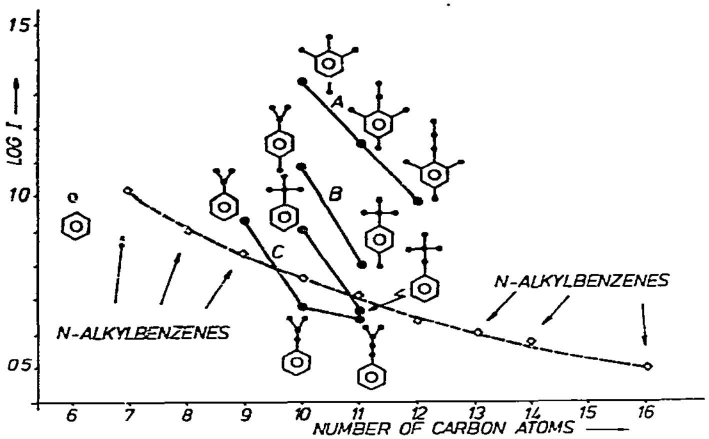

Fig. 5. Dependence of log *I* on number of carbon atoms for alkylbenzenes with extension of the alkyl chain placed between two *ortho*-substituted methyl groups (curve A), for alkylbenzenes when *tert.*-butyl replaces isopropyl (curve B) and isobutyl replaces isopropyl (curve C).

The introduction of another methyl group into a *meta*-position has little effect on the retention data, *e.g.*, in the series toluene–*m*-xylene–1,3,5-trimethylbenzene or for the pairs ethylbenzene–*m*-ethyltoluene, *o*-xylene–1,2,4-trimethylbenzene and 1,2,3-trimethylbenzene–isodurene.

The effects of *ortho*, and *meta*-substitution are illustrated schematically in Fig. 6.

Number and shape of alkyls

Alkylbenzenes with identical molecular masses do not form a group which would be separable as a whole, but on the contrary individual members cover the whole range of retention data.

Generally, higher retention data are found for alkylbenzenes with short alkyl groups (especially methyl) and the *ortho*-effect takes place here. With increasing length of the alkyl group, the effect of the longer chain is more substantial and/or the *ortho*-effect is disturbed, retention times being decreased.

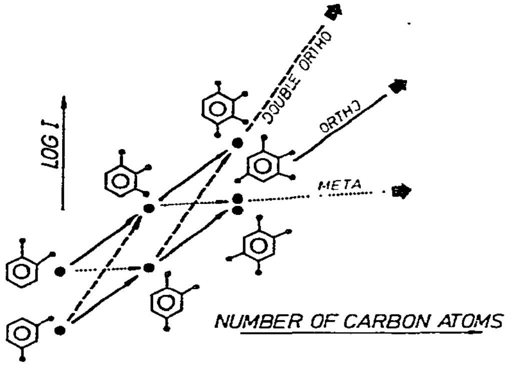

Fig. 6. Effect of *ortho* and *meta* substitution on chromatographic behaviour of alkylbenzenes.

When comparing alkylbenzenes having one alkyl group and the same number of carbon atoms, it is evident that compounds having an alkyl chain branched at the α-carbon atom are more strongly retarded. For example, the retention times of isopropylbenzene and *tert.*-butylbenzene are longer than those of n-C_3 and n-C_4, or even than of ethylbenzene. Cyclopentylbenzene ($\log I = 0.994$) also belongs to this group. On the other hand, if the alkyl chain is branched at the β-carbon atom (or on further carbon atoms), the retention time decreases, *e.g.*, when comparing isobutylbenzene with n-C_4 and neopentylbenzene with n-C_5. In the case of 2-methyl-3-phenylbutane, where the chain is branched at both α and β carbon atoms, there is strong retardation, probably as a result of the mutual arrangement of the alkyl group and the benzene ring.

REFERENCES

1 M. Popl, J. Mostecký, V. Dolanský and M. Kuraš, *Anal. Chem.*, 43 (1971) 518.
2 M. Popl, V. Dolanský and J. Mostecký, *J. Chromatogr.*, 91 (1974) 649.
3 J. C. Suatoni, H. R. Garber and B. E. Davies, *J. Chromatogr. Sci.*, 13 (1975) 367.
4 M. Popl, J. Čoupek and S. Pokorný, *J. Chromatogr.*, 104 (1975) 135.
5 M. Popl, V. Dolanský and J. Mostecký, *J. Chromatogr.*, 117 (1976) 117.
6 A. N. Ageev, A. V. Kiselev and Y. I. Yashin, *Dokl. Akad. Nauk SSSR*, 249 (1979) 377.
7 R. M. Smith, *J. Chromatogr.*, 209 (1981) 1.
8 M. M. Kuraš, J. Kříž, J. Tříska and L. Vodička, *J. Chromatogr.*, 191 (1980) 319.
9 M. Kuraš, J. Kříž, L. Vodička and M. Březina, *Fresenius' Z. Anal. Chem.*, 299 (1979) 375.
10 W. Boehme and H. Engelhardt, *J. Chromatogr.*, 133 (1977) 67.