

CHROM. 7818

GEL PERMEATION CHROMATOGRAPHY OF ALKYL BENZENES

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(Received July 9th, 1974)

SUMMARY

Elution volumes relative to the elution volume of benzene were investigated in the gel chromatography of alkylbenzenes, benzene derivatives with condensed rings and benzene derivatives containing an alkyl side-chain. The dependence of the relative elution volume on the number of substituents and on the total number of alkyl carbon atoms was determined for polysubstituted alkylbenzenes. The elution volumes of benzene derivatives with condensed rings are discussed in relation to their structure.

INTRODUCTION

Gel permeation chromatography¹⁻³ (GPC) is being increasingly used for the investigation of the fractionation and identification of complex hydrocarbon mixtures, such as oil distillates, crude oil residues and asphalts, as it makes possible further fractionation in those cases where the separation methods used so far, particularly adsorption chromatography, have proved unsatisfactory. An example of such a fractionation is given in papers by Coleman *et al.*⁴ and Hirsch *et al.*⁵, in which crude oil fractions freed from polar compounds were separated by adsorption chromatography into three fractions consisting of mono-, di- and polyaromatic compounds. The fractions were further fractionated by GPC into several other fractions, which were studied by mass and nuclear magnetic resonance spectrometry. It follows from their work that, for instance, in the fraction of monoaromatics, alkylbenzenes have the smallest GPC elution volumes, while benzenes with condensed rings are eluted from the column last.

So far, no survey has been published that contains the necessary data for predicting elution volumes of all types of hydrocarbons that might appear in aromatic fractions. A paper by Hendrickson and Moore⁶ gives results for alkylbenzenes with alkyl groups containing up to three carbon atoms and for tetralin. Data published by Oelert⁷ and Oelert and Weber⁸ are more detailed, but compounds such as cycloaromatic hydrocarbons with a side-chain and polysubstituted benzene derivatives

were not investigated. The effect of the elution agent in the GPC of polycondensed aromatic hydrocarbons was studied by Bergmann *et al.*⁹. Some alkylbenzenes were used as model compounds in the GPC investigations of phenols in tetrahydrofuran¹⁰.

This paper deals with measurements of the elution volumes of monoaromatics on the styrene-divinylbenzene gel S-gel-832 with tetrahydrofuran as the elution agent. Monoaromatics were chosen because in this field it was possible to provide a sufficient number of standard compounds. It may be assumed that, after generalization of the results, it will be possible to predict the chromatographic behaviour of diaromatics.

EXPERIMENTAL

The measurements were carried out on a gel chromatograph built at the Institute of Macromolecular Chemistry of the Czechoslovak Academy of Sciences, using five stainless-steel columns of dimensions 1200×8 mm packed with the styrene-divinylbenzene copolymer S-gel-832 with an exclusion limit of molecular weight 1000. The compounds used in the measurements were dissolved in tetrahydrofuran to give a *ca.* 5% solution and a volume of 0.3–0.4 ml was injected into the first column.

The measured elution volumes, V_e (ml), were recalculated to corrected elution volumes, V_k (ml), by subtracting the void volume, $V_o = 128.4$ ml. The contributions of an alkyl carbon atom, $\log V_R/nC_A$, were calculated as the difference between the logarithms of the corrected elution volume of the compound and the corrected elution volume of benzene divided by the number of the carbon atoms in the alkyl group. For benzene derivatives with condensed rings, a similar expression was used, namely $\log V_R/nC_N$, where nC_N is the number of naphthenic carbon atoms.

It is easy to see that from the contribution of the alkyl carbon atom one can readily obtain the elution volume of the compound relative to benzene, V_R , by multiplying it by the number of the alkyl carbon atoms and by taking the antilogarithm.

For benzene derivatives with condensed rings containing an alkyl side-chain, the total contribution consists of contributions of naphthenic and those of alkyl carbon atoms. It was assumed in the calculations that the contribution of naphthenic carbon atoms was the same as in the basic cycloaromatic hydrocarbon. Thus, for instance, in the case of 5-ethylindane, the contribution of the naphthenic carbon atoms was assumed to be the same as in indane, and only the contribution of the ethyl group was added.

RESULTS AND DISCUSSION

According to the data in Table I, monoaromatics can be divided into three main groups:

I, alkylbenzenes;

II, benzenes with condensed rings;

III, benzenes with condensed rings and with an alkyl side-chain.

The alkylbenzenes in Group I have the smallest elution volumes of all groups with the same number of non-aromatic carbon atoms in the molecule (Fig. 1). Also, the elution volumes do not depend significantly on the shape of the alkyl group, as shown by comparison of *n*-amylbenzene and neopentylbenzene; nor do they depend on the number of substituents in the benzene ring (one or two), which is shown by the

TABLE I
ELUTION DATA FOR ALKYL BENZENES

$V_D = 128.4$ ml.

Compound	V_c	nC_A	nC_N	$\log V_R$	$\log V_R$
				nC_A	nC_N
Benzene	263.8	0	0	0	0
Toluene	252.7	1	0	-0.038	
<i>n</i> -Propylbenzene	238.8	3	0	-0.030	—
Isopropylbenzene	239.4	3	0	-0.029	—
<i>n</i> -Amylbenzene	228.2	5	0	-0.026	—
Neopentylbenzene	227.7	5	0	-0.027	—
<i>m</i> -Diisopropylbenzene	223.3	6	0	-0.026	—
<i>n</i> -Heptylbenzene	219.0	7	0	-0.025	—
<i>n</i> -Decylbenzene	206.4	10	0	-0.024	—
<i>m</i> -Xylene	250.0	2	0	-0.023	—
<i>m</i> -Ethyltoluene	242.9	3	0	-0.024	—
<i>p</i> -Isopropyltoluene	234.5	4	0	-0.026	—
<i>p-tert.</i> -Butyltoluene	229.0	5	0	-0.026	—
1,3,5-Trimethylbenzene	246.2	3	0	-0.020	—
1,2,4,5-Tetramethylbenzene	243.7	4	0	-0.017	—
Pentamethylbenzene	246.7	5	0	-0.012	—
Hexamethylbenzene	246.2	6	0	-0.010	—
Hexaethylbenzene	214.6	12	0	-0.016	—
Indane	257.9	0	3	—	-0.006
5-Methylindane	253.2	1	3	-0.016	-0.006
5-Ethylindane	247.2	2	3	-0.019	-0.006
Tetralin	255.1	0	4	—	-0.007
6-Methyltetralin	250.5	1	4	-0.016	-0.007
Tetrahydroacenaphthene	253.5	0	6	—	-0.006
1,2,3,4,5,6,7,8-Octahydroanthracene	252.4	0	8	—	-0.005
Decahydropyrene	249.7	0	10	—	-0.005

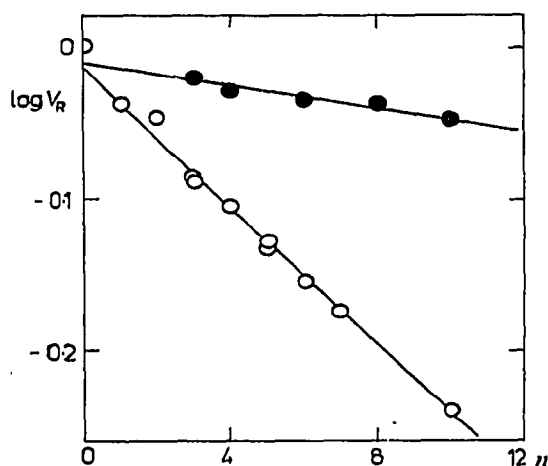


Fig. 1. Dependence of the relative elution volume ($\log V_R$) on the number of non-aromatic carbon atoms in the molecule (n). ○, Alkylbenzenes; ●, benzenes with condensed rings without side-chains.

elution volume of *n*-diisopropylbenzene corresponding to the expected elution volume of *n*-hexylbenzene. If the benzene ring contains three or more short alkyl substituents, the elution volumes increase. This is clearly shown by polymethylbenzenes, for which the elution volume decreases with increasing number of methyl substituents only up to the tetramethyl derivative, attaining a value corresponding approximately to that of 2.5 carbon atoms in a straight alkyl chain, while the elution volumes of the penta- and hexamethyl derivatives slightly increase.

Minor deviations from the calculated values of the elution volume are observed for a series of dialkylbenzenes with methyl as one of the alkyl groups. Here the greatest difference occurs for *m*-xylene; it decreases with increasing length of the first alkyl group, so that *p*-*tert*-butyltoluene can be correlated with the amylbenzenes.

The results for hexaethylbenzene also show that a higher elution volume than the calculated value is found. This substitution effect can generally be expressed in such a manner that the elution volumes increase in comparison with the theoretical value relative to the number of substituents and with decreasing average length of the alkyl group.

It was deduced from the results that for the system used the following relationship would be valid for polysubstituted alkylbenzenes:

$$\log V_R = 5.3 \cdot 10^{-4} x^3 - 2.51 \cdot 10^{-2} nC_A$$

where V_R is the elution volume of the compound relative to the elution volume of benzene, x is the number of substituents and nC_A is the total number of alkyl carbon atoms. The experimental data satisfy this equation well, with the exception of hexamethylbenzene, which represents a major deviation.

Contributions for the alkyl carbon atom are regular from propylbenzene to decylbenzene. The correlation of data for monoalkylbenzenes within the range $nC_A = 3-10$ (from propylbenzene to decylbenzene) yielded an average value of $\log V_R/nC_A = -0.0267$.

In contrast with group I, benzene derivatives with condensed rings without side-chains (group II) have the largest elution volumes of all monoaromatics with the same number of non-aromatic carbon atoms. It should be stressed that the contribution of a carbon atom in the ring corresponds approximately to 20% of the contribution of a carbon atom in the aliphatic chain. The correlation of contributions for the naphthenic carbon atoms in the range $nC_N = 3-10$ (from indane to decahydropyrene) gave an average value of $\log V_R/nC_N = -0.0058$. It seems from the data measured that it makes no difference whether the rings form a compact molecule, as in the case of decahydropyrene, or whether they are isolated, as in the case of 1,2,3,4,5,6,7,8-octahydroanthracene. The results also do not allow one to conclude that the contribution of a carbon atom in a five-membered ring (indane, tetrahydroacenaphthene) would be essentially different from that of a carbon atom in the six-membered cyclanes.

Group III compounds, benzenes with condensed rings with a side-chain, occupy the area in Fig. 1 between the straight lines representing group I and II compounds. According to the limited data on the three compounds at our disposal, one can see that the contribution of an alkyl carbon atom in the side-chain in this type of compound is only slightly less than or the same as that for compounds of group I.

It is likely that for compounds with the alkyl groups situated on larger molecules, such as octahydroanthracene and decahydrophyrene, the steric order effect will become operative, that is, the alkyl groups situated on opposite parts of the molecule will reduce the elution volumes more than those situated in *ortho* positions with respect to each other. A similar effect has been observed for *p*- and *o*-xylene⁶, and it may be expected also to become operative in the GPC of cyclic compounds.

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