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QUALITATIVE GAS CHROMATOGRAPHIC ANALYSIS AND DETERMINATION OF SOLUTE PROPERTIES

CALCULATION OF THE RETENTION INDICES OF BENZENE HOMOLOGUES ON SQUALANE

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SUMMARY

An equation for the accurate and simple calculation of the theoretical retention indices of benzene homologues on squalane is proposed. The equation permits the calculation of the retention index at different temperatures, so that one can choose the optimal separation temperature, and the determination of the changes of solute pressure with temperature.

INTRODUCTION

In gas chromatography, the prediction of separation and peak identification could be considered as direct problems. The determination of vapour pressure (p^0) and its temperature dependence [$\log p^0 = f(T)$], boiling point (t_b) and density [d_4^{20}], and also the determination of other solute properties, from retention data are problems of an indirect nature. The possibility of the solution of both types of problem for hydrocarbons was discussed previously^{1,2} and an improved equation for the calculation of the retention indices of isoalkanes has been proposed³:

$$I^{\text{theor}} = PCI + SN \quad (1)$$

The first term (PCI) connects the retention at different temperatures with the p^0 and molecular volume (V_m) of the solute. The second term, the structural number (SN), expresses the change in entropy of a compound on dissolution in a non-polar phase. Its value is determined on the basis of the different structural elements of the solute molecule. Their influence depends on the phase used, however, and estimations of the various parameters are different for different stationary phases.

The aim of this work was to derive a simple equation for the calculation of

I^{theor} and SN for benzene homologues dissolved in squalane on the basis of the correlation analysis of the influence of their different structural elements and their PCI values.

CALCULATION

Although a computer can be used to solve various calculations, the formality of some solutions could impede an understanding of the character of the process being studied. Our investigation was based on the theoretical assumption from the previous work³ and we considered the retention of benzene homologues in the same manner. Many different structural elements were examined, and a simple expression for calculation was derived.

A Fortran program for the calculation of the regression coefficients of the different structural elements was used. After determining the most significant influences, the following structural elements (X_i) were chosen for further investigation: n_0 , the number of carbon atoms in all alkyl substituents (R); n_R , the number of R; n_t , the number of tertiary carbon atoms in R; n_q , the number of quaternary carbon atoms in R; r , the distance (in number of carbon atoms) between the aromatic cycle and branched carbon atom in R; n_{CH_3} , the number of methyl groups in the branch; n_b , the number of carbon atoms in the whole branched R; r_b , the number of carbon atoms in R left after forming the first n -butane chain; n_v , the number of vacant positions in the aromatic cycle, bearing in mind the symmetry of the molecule; and n_b^o , the number of branched carbon atoms in *ortho*-positions.

A correlation coefficient of greater than 0.98 for the linear equation

$$SN = A + \sum B_i X_i \quad (2)$$

was achieved by using these factors (A and B are constants).

Several combinations of the significant structural elements were examined and we succeeded in combining all elements connected with the structure of the substituent R in one factor, X_1 , and those related to its location in the cycle in other factor, X_2 :

$$SN = A + B_1 X_1 + B_2 X_2 \quad (3)$$

where

$$X_1 = n_0 + n_R + n_t + 2n_q + r - \frac{n_{\text{CH}_3}}{n_b} - 2r_b \quad (4)$$

and

$$X_2 = n_v + n_b^o \quad (5)$$

Some examples of the values of X_1 and X_2 obtained for different benzene homologues are given in Table I.

TABLE I

NUMBER OF DIFFERENT STRUCTURAL ELEMENTS IN SOME AROMATIC HYDROCARBONS AND CORRESPONDING VALUES OF X_1 AND X_2

No.	Hydrocarbon	n_o	n_R	n_t	n_q	r	n_{CH_3}/n_b	r_b	X_1	n_v	n_b^o	X_2
1	<i>n</i> -Amylbenzene	5	1	0	0	0	0	2	4	0	0	0
2	<i>p</i> -Diethylbenzene	4	2	0	0	0	0	0	6	2	0	2
3	Isobutylbenzene	4	1	1	0	1	1/4	0	6.75	0	0	0
4	<i>sec.</i> -Butylbenzene	4	1	1	0	0	1/4	0	5.75	0	0	0
5	<i>tert.</i> -Butylbenzene	4	1	0	1	0	2/4	0	6.5	0	0	0
6	1-Methyl-3- <i>n</i> -propylbenzene	4	2	0	0	0	0	0	6.0	3	0	3
7	<i>o</i> -Diisopropylbenzene	6	2	2	0	0	$2 \times 1/3$	0	9.33	4	2	2
8	1,2,4-Trimethylbenzene*	3	3	0	0	0	0	0	6.0	4	0	4
9	1,3-Dimethyl-5-ethylbenzene*	4	3	0	0	0	0	0	7.0	3	0	3
10	1,3-Dimethyl-2-ethylbenzene*	4	3	0	0	0	0	0	7.0	9	0	9

* In trisubstituted benzene homologues, n_o is determined by the presence of the most influenced *ortho*-positions, enhanced by the number of symmetrical areas.

RESULTS AND DISCUSSION

The *SN* values calculated according to eqn. 3 for different mono-, di- and tri-substituted benzene homologues and the differences (Δ) between I_{exp}^o and I^{theor} are given in Table II.

When mono- and disubstituted benzene homologues only are considered, the variance (s^2) of Δ is ± 1.2 i.u. This value is statistically equal to the variance of retention indices obtained experimentally. The inclusion of trisubstituted benzene homologues increases the variance of Δ to ± 2 i.u., but no difference is greater than 4 i.u.

A comparison of the linear equations for *SN* of isoalkanes (eqn. 6) and aromatic hydrocarbons (eqn. 7)

$$SN = 5.23 + 1.8n_b + 1.7n_{CH_3} + n - 3n_o + 2n_t \quad (6)$$

$$SN = -47.3 + 5.7n_o + 3n_R + 2n_t + 2n_q + 5r + 9n_{CH_3} + 3.5n_b - 3.2r_b - 1.9n_v + 1.9n_b^o \quad (7)$$

as well as the more simple equations for isoalkanes

$$SN = -1.8 + 0.9X_1 + 7.7X_4 \quad (8)$$

and for aromatic hydrocarbons

$$SN = -45.8 + 3.39X_1 - 1.54X_2 \quad (9)$$

shows the important role that a non-polar phase such as squalane could play in the retention of different types of hydrocarbons. The value of the uncombined term A in the equations related to the benzene homologues is greater by one order of magnitude

TABLE II

SN VALUES OF BENZENE HOMOLOGUES AND Δ BETWEEN I_{exp}^{10} AND I^{theor}

No.	Hydrocarbon	SN	I^{theor}	I_{exp}^{10}	Δ
1	Benzene	-46.2	652.0	652.4 (110°)	0.4
2	Toluene	-38.0	758.1	757.1 (100°)	-1.0
3	Ethylbenzene	-37.1	846.0	847.4 (100°)	1.4
4	<i>n</i> -Propylbenzene	-32.5	936.1	936.3 (100°)	0.2
5	<i>n</i> -Butylbenzene	-31.0	1034.3	1036.4 (100°)	2.1
6	<i>n</i> -Amylbenzene	-32.3	1137.6	1137.6 (100°)	0.0
7	<i>n</i> -Hexylbenzene	-36.8	1234.1	1235.5 (100°)	1.1
8	Isopropylbenzene	-31.1	905.6	906.7 (100°)	1.1
9	Isobutylbenzene	-22.2	990.5	989.8 (100°)	-0.7
10	<i>sec</i> -Butylbenzene	-26.7	989.4	989.8 (100°)	0.4
11	<i>tert</i> -Butylbenzene	-25.1	972.0	973.3 (100°)	1.3
12	<i>p</i> -Xylene	-32.5	866.5	863.7 (110°)	-2.8
13	<i>m</i> -Xylene	-35.4	866.7	865.2 (110°)	-1.5
14	<i>o</i> -Xylene	-39.9	885.3	886.8 (110°)	1.5
15	1-Methyl-4-isopropylbenzene	-26.2	1014.0	1013.9 (110°)	-0.1
16	1-Methyl-3-isopropylbenzene	-26.9	1006.4	1005.5 (110°)	-0.9
17	1-Methyl-2-isopropylbenzene	-26.6	1023.8	1022.6 (110°)	-1.2
18	1,4-Diisopropylbenzene	-16.9	1159.4	1159.0 (100°)	-0.4
19	1,3-Diisopropylbenzene	-18.7	1126.1	1126.0 (100°)	-0.1
20	1,2-Diisopropylbenzene	-17.3	1132.0	1132.0 (100°)	0.0
21	1-Methyl-4- <i>n</i> -propylbenzene	-26.3	1039.1	1036.8 (92°)	-2.3
22	1-Methyl-3- <i>n</i> -propylbenzene	-27.9	1033.5	1031.4 (92°)	-2.1
23	1-Methyl-2- <i>n</i> -propylbenzene	-31.1	1044.1	1043.6 (92°)	-0.5
24	1-Methyl-4-ethylbenzene	-30.3	953.5	951.9 (100°)	-1.6
25	1-Methyl-3-ethylbenzene	-31.8	951.2	949.5 (100°)	-1.7
26	1-Methyl-2-ethylbenzene	-35.4	965.4	965.8 (100°)	0.4
27	1,4-Diethylbenzene	-28.8	1038.8	1039.0 (92°)	0.2
28	1,3-Diethylbenzene	-30.4	1027.7	1028.0 (92°)	0.3
29	1,2-Diethylbenzene	-31.1	1039.5	1039.0 (92°)	-0.5
30	1,3,5-Trimethylbenzene	-31.9	965.8	967.6 (100°)	1.8
31	1,3-Dimethyl-5-ethylbenzene	-24.5	1050.4	1048.2 (100°)	-2.2
32	1,2,4-Trimethylbenzene	-32.4	987.4	988.2 (100°)	0.8
33	1,2-Dimethyl-4-ethylbenzene	-32.3	1067.9	1072.0 (100°)	4.1
34	1,4-Dimethyl-2-ethylbenzene	-27.4	1059.3	1060.0 (100°)	0.7
35	1,3-Dimethyl-4-ethylbenzene	-30.0	1064.8	1066.6 (100°)	0.7
36	1,2,3-Trimethylbenzene	-43.0	1011.3	1011.9 (100°)	1.8
37	1,2-Dimethyl-3-ethylbenzene	-39.3	1087.8	1088.1 (100°)	0.3
38	1,2-Dimethyl-2-ethylbenzene	-35.5	1072.4	1072.0 (100°)	-0.4

 $s^2 = 1.97$

than that of B_i in eqn. 2 and the uncombined term in the equations for the isoalkanes.

The accuracy of the calculation of SN and I^{theor} was examined by calculating p^0 and t_b for some benzene homologues. Examples of calculated p^0 values are given in Table III.

The calculation of t_b is made according to the transformed Antoine equation:

$$t_b = \frac{B}{A - 2.8808} - C$$

TABLE III

COMPARISON OF p^0 (mmHg) CALCULATED AT 100° AND TAKEN FROM THE LITERATURE

No.	Hydrocarbon	$p^0_{calc.}$	$p^0_{lit.}$	Reference
1	Benzene	1349	1351	4
2	Toluene	552.5	556.31	4
3	Ethylbenzene	259.3	256.95	4
4	<i>n</i> -Propylbenzene	124.7	124.73	4
5	<i>n</i> -Butylbenzene	56.67	55.89	4
6	<i>n</i> -Amylbenzene	24.85	24.83	4
7	<i>n</i> -Hexylbenzene	11.20	11.13	5
8	<i>tert.</i> -Butylbenzene	92.10	91.26	4
9	1-Methyl-4-ethylbenzene	112.2	113.4	4
10	1-Methyl-3-ethylbenzene	113.3	114.59	4
11	1-Methyl-2-ethylbenzene	101.9	101.58	4
12	1-Methyl-4- <i>n</i> -propylbenzene	55.09	56.35	6
13	1-Methyl-3- <i>n</i> -propylbenzene	57.32	58.11	6
14	1-Methyl-2- <i>n</i> -propylbenzene	52.54	52.89	6
15	1-Methyl-4-isopropylbenzene	66.16	65.8	4
16	1-Methyl-3-isopropylbenzene	72.74	73.24	5
17	1-Methyl-2-isopropylbenzene	67.0	69.02	5

where 2.8808 is $\log p$ at 760 mmHg. As an example, the boiling point of 1-methyl-4-ethylbenzene was calculated. The values of I_{exp} needed were taken from different literature sources and were as follows: 86°, 948; 92°, 950; 100°, 952.3 and 951.9; 110°, 953.9 and 953.5; 118°, 955.6 and 955.1. These data could be used in two ways:

(1) calculation of p^0 at all temperatures available ($t_b = 160.4$); (2) estimation of the temperature dependence of I_{exp} , and then calculation of three p^0 values only ($t_b = 161.1^\circ$). The boiling point of 1-methyl-4-ethylbenzene is 161.99°.

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