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QUALITATIVE GAS CHROMATOGRAPHIC ANALYSIS AND DETERMINATION OF SOLUTE PROPERTIES

STUDY OF THE RELATIONSHIP BETWEEN THE MOLECULAR STRUCTURE AND GAS CHROMATOGRAPHIC RETENTION OF ALKENES ON SQUALANE

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SUMMARY

The relationship between the molecular structure, vapour pressure and molecular volume of alkenes and their gas chromatographic retention on squalane was studied. An equation with a correlation coefficient of 0.84 was derived:

$$I_t^{\text{theor}} = PCI_t - A + B \left(\frac{n_{\text{CH}_3} + n_t - n_R}{n_0 - n_a} + \frac{n_C^S}{n_C^L} \right)$$

The retention indices of 62 olefins calculated with this equation showed a very good correlation with the experimental values. The dispersion for the basic group of 49 olefins is 2.0 i.u. and the average deviation for the whole group of 62 olefins is ± 2.1 i.u.

INTRODUCTION

Experimental Kováts retention indices^{1,2} I_{exp} are widely used in gas chromatography for the identification of chromatogram peaks, especially for hydrocarbon mixtures. Retention indices obtained with good accuracy for a large number of isoalkanes, naphthenes and aromatic hydrocarbons are given in the literature, but there are considerably fewer data for olefins³⁻⁷, and the values obtained by different workers show substantial differences. As it is known⁸ for an increasing of the certainty of qualitative analysis, several methods have been developed for calculation of retention index. In particular, methods for the calculation of the retention indices of olefins on squalane were discussed by Schomburg⁹, who applied the homomorphic factor. Ladon¹⁰ used an equation relating the retentions on two stationary phases to determine

the class to which a given solute belongs. Soják and co-workers found a relationship between the boiling points and retention indices of C₉, C₁₀ (ref. 11), C₁₁ (ref. 12) and C₁₂ (ref. 13) alkenes. Takacs *et al.*¹⁴ proposed an additive method for calculating retention indices on the basis of the molecular structure of unsaturated hydrocarbons and compared them with the experimental values.

This paper applies the concept of the relationship between the vapour pressure, molecular volume, structure and retention to olefins, a more detailed consideration of which was given in previous papers¹⁵⁻¹⁷. This investigation was carried out in order to obtain an equation not only for the calculation of retention indices of olefins on squalane at different temperatures, but also for a simple precise determination of vapour pressure and its change with the temperature. Thus, the use of gas chromatographic data for measuring physico-chemical properties of the solutes could have the same or even greater success than the commonly used physico-chemical methods.

CALCULATION

The influence of the different structural elements of olefins was studied as described previously¹⁷. Many 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. Structural number¹⁷ was expressed as a linear equation and correlation analysis was used to choose the most important elements. An eight-term equation was formulated as a result:

$$y = b_0 + b_1 x_1 + b_2 x_2 + b_3 x_3 + b_4 x_4 + b_5 x_5 + b_6 x_6 + b_7 x_7 \quad (1)$$

where

y = difference between experimental retention index, I , and the calculated physico-chemical index, PCI ;

b_i and x_i = parametric values of the following structural elements ($i = 0-7$):

x_1 = number of methyl groups in the alkene, n_{CH_3} ;

x_2 = number of tertiary carbon atoms in the olefin, n_t ;

x_3 = number of substituents, n_R ;

x_4 = number of quaternary carbon atoms in the olefin, n_q ;

x_5 = total number of carbon atoms in the solute, n_0 ;

x_6 and x_7 = number of the carbon atoms from both sides of the π -electron plane.

x_6 is determined by the number of carbon atoms in the shorter chain, n_C^S , and x_7 by the number of carbon atoms in the longer chain, n_C^L .

The computerized solution of this equation gives the following:

$$y = -7.40 - 1.69x_1 + 0.09x_2 + 1.04x_3 + 1.38x_4 + 1.25x_5 - 1.89x_6 + 0.08x_7$$

Correlation analysis shows that each parameter has an independent influence and that all of the structural elements used make a contribution, because the correlation coefficient decreases considerably when any one of the structural elements is omitted.

Several combinations of the significant structural elements were examined in order to formulate a simple equation for calculation, and we succeeded in combining all of the elements in the following equation:

$$SN = A + BX \quad (2)$$

where

$$X = \frac{n_{\text{CH}_3} + n_t - n_R}{n_o - n_a} + \frac{n_C^S}{n_C^L} \quad (3)$$

As an example, the value of X for 4-methyl-*cis*- and -*trans*-pentene-2 will be calculated:

4-Methyl-*cis*-pentene-2: $n_{\text{CH}_3} = 3$; $n_t = 3$; $n_R = 1$; $n_o = 6$; $n_a = 0$; $n_C^S = 0$; $n_C^L = 4$.

$$X = \frac{3 + 3 - 1}{6 - 0} + \frac{0}{4} = 0.83$$

4-Methyl-*trans*-pentene-2: $n_{\text{CH}_3} = 3$; $n_t = 3$; $n_R = 1$; $n_o = 6$; $n_a = 0$; $n_C^S = 1$; $n_C^L = 3$.

$$X = \frac{3 + 3 - 1}{6 - 0} + \frac{1}{3} = 1.16$$

Literature values of I for 49 alkenes^{3,4} were used for calculation of SN according to eqn. 2. The differences between the experimental and calculated values showed, in contrast to the saturated hydrocarbons studied previously¹⁷, a slight dependence on temperature. In this paper, no further attention is paid to this phenomenon and an average value for SN in the temperature range 30–70° was calculated. The PCI values of the olefins studied were calculated from the densities^{18–20} and vapour pressures^{20,21}. The results are given in Table I. An attempt to extend the validity of eqn. 2 was made, calculating the SN , PCI and I^{theor} values for 13 higher C₇–C₈ olefins. The results obtained are given in Table II.

RESULTS AND DISCUSSION

The results in Table I show that the greater the number of carbon atoms in the members of one homologous series, the lower is the value of SN , which could explain the approximation of the values of the variances (s^2) in Table II. It could be assumed that the longer the chain of the olefin, the smaller is the difference in the entropy of solution of n -alkanes and olefins. The values of SN (Table I) also show that *trans*-isomers are dissolved in the stationary phase with greater difficulty than *cis*-isomers, because the latter have an SN value about twice as small.

A comparison of the differences between I_{exp} and PCI and between I_{exp} and I^{theor} , and especially the corresponding variances s^2 given in Table I, shows, that I^{theor}

TABLE I

DIFFERENCES Δ_1 BETWEEN THE I AND PCI VALUES OF C_5 - C_8 ALKENES (AVERAGE FOR THE TEMPERATURE RANGE 30-70°) AND Δ_2 BETWEEN I AND I^{thcor}

No.	Hydrocarbon	Δ_1	Δ_2
1	<i>cis</i> -Pentene-2	-5.4	1.2
2	<i>trans</i> -Pentene-2	-7.1	0.3
3	4-Methyl- <i>cis</i> -pentene-2	-4.2	0.2
4	4-Methyl- <i>trans</i> -pentene-2	-6.6	0.6
5	<i>cis</i> -Hexene-3	-5.1	1.5
6	<i>trans</i> -Hexene-3	-7.8	0.8
7	<i>cis</i> -Hexene-2	-4.2	0.6
8	<i>trans</i> -Hexene-2	-5.7	0.5
9	<i>cis</i> -Butene-2	-5.6	0.4
10	<i>trans</i> -Butene-2	-10.8	0.5
11	<i>cis</i> -Heptene-3	-2.4	0.7
12	<i>trans</i> -Heptene-3	-4.8	1.6
13	4-Methyl- <i>cis</i> -hexene-2	-2.8	1.0
14	4-Methyl- <i>trans</i> -hexene-2	-5.8	0.8
15	2-Methyl- <i>trans</i> -hexene-3	-8.7	1.5
16	3-Methyl- <i>cis</i> -hexene-2	-6.2	2.2
17	5-Methyl- <i>trans</i> -hexene-2	-5.1	0.1
18	4,4-Dimethyl- <i>trans</i> -pentene-2	-5.3	0.5
19	2,2-Dimethyl- <i>trans</i> -hexene-3	-8.2	1.7
20	3,4,4-Trimethyl- <i>cis</i> -pentene-2	-1.5	1.2
21	<i>trans</i> -Heptene-2	-1.7	2.6
22	3,4-Dimethylpentene-1	-1.6	1.5
23	2-Methyl- <i>trans</i> -heptene-3	-6.1	1.7
24	Pentene-1	-4.5	2.3
25	Hexene-1	-3.6	1.7
26	Heptene-1	-3.2	1.5
27	Octene-1	-2.9	1.4
28	3-Methylbutene-1	-6.5	3.3
29	2-Methylpentene-2	-4.4	3.3
30	2-Methylbutene-2	-2.8	1.2
31	2-Methylbutene-1	-2.8	1.3
32	2-Methylpentene-1	-2.0	0.8
33	4-Methylpentene-1	-1.3	1.4
34	2-Ethylbutene-1	-1.0	0.2
35	3-Methylpentene-1	-0.8	1.9
36	2-Methylhexene-1	-0.2	0.8
37	3-Ethylpentene-1	-1.2	1.2
38	2-Methylhexene-2	-0.8	1.9
39	3-Methylhexene-1	-3.0	0.6
40	5-Methylhexene-1	-3.5	1.1
41	4-Methylhexene-1	-1.2	1.2
42	2,3-Dimethylbutene-2	-2.3	0.4
43	2,3-Dimethylbutene-1	-0.6	1.6
44	2,4-Dimethylpentene-2	-5.4	1.8
45	2,3-Dimethylpentene-1	-1.2	0.7
46	3-Methyl 2-ethylbutene-1	-1.1	0.8
47	2,3-Dimethylhexene-1	-1.2	0.5
48	2,5-Dimethylhexene-2	-1.6	1.5
49	2,4,4-Trimethylpentene-2	-1.8	1.8

$$s^2 = 20.5 \quad s^2 = 2.06$$

TABLE II

DIFFERENCES Δ_1 BETWEEN THE I AND PCI VALUES OF C_7 - C_8 ALKENES (AVERAGE FOR THE TEMPERATURE RANGE 30-70°) AND Δ_2 BETWEEN I AND I^{theor}

No.	Hydrocarbon	Δ_1	Δ_2
1	3-Ethylpentene-2	+1.8	3.4
2	2,4,4-Trimethylpentene-1	+5.6	4.6
3	2,3-Dimethylhexene-2	+3.5	3.9
4	2,2-Dimethyl- <i>cis</i> -hexene-3	+0.9	2.9
5	2,3,4-Trimethylpentene-2	+0.8	2.4
6	3,3-Dimethylpentene-1	+0.4	0.8
7	2,3,3-Trimethylbutene-1	+4.2	3.7
8	2,4-Dimethylpentene-1	+0.3	0.7
9	3,3-Dimethylbutene-1	+0.3	1.2
10	2,3-Dimethylpentene-2	+1.3	2.2
11	4,4-Dimethylpentene-1	+3.1	3.5
12	2-Methyl-3-ethylpentene-2	+3.0	3.4
13	2-Methyl-3-ethylpentene-1	+4.2	4.3
		$s^2 = 8.7$	$s^2 = 10.4$

is much more correct than PCI , and has a deviation of ± 2.0 i.u., which is the same as that for the experimental data.

The statistical evaluation shows $F_{(49,30)} = 2.21$ and the tabular $F_{(50,30)} = 2.24$. The value 2.21 for this Fischer criteria represents the relationship between s^2 for the olefins (in Table I) and s^2 for 30 olefins for which I^{exp} values are quoted in the literature^{3,4,7}. A comparison using F criteria with the variance obtained from the retention indices calculated according to Takacs *et al.*¹⁴ was also made. We did not take into consideration in this comparison 12 olefins that give differences between values calculated according to Takacs *et al.*¹⁴ and the experimental values of more than 15 i.u. $F_{(46,62)} = 3.14$ and tabular $F_{(50,60)} = 1.87$. The value 3.14 represents the relationship between s^2 for 46 differences between I_{exp} and I calculated according to Takacs *et al.*¹⁴ and s^2 for 62 differences between I_{exp} and I^{theor} calculated by using eqn. 2. The extension of the application of eqn. 2 to C_7 - C_8 olefins (Table II) shows, however, that the precisions of PCI and I^{theor} become equal.

The comparisons according to Fischer show that the proposed method has very good accuracy. In addition, compared with the experimental method, the accuracy and the simple calculations involved make the proposed method suitable for analytical purposes, as well as for the calculation of physico-chemical data.

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