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CALCULATION OF THE RETENTION INDICES OF C_5–C_9 CYCLOALKANES ON SQUALANE

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SUMMARY

The relationship between molecular structure, vapour pressure and molecular volume of 30 C_5–C_9 cycloalkanes and their gas chromatographic retention on squalane were investigated. An equation for the accurate and simple calculation of their theoretical retention indices is proposed. The equation permits the calculation of the vapour pressures of these hydrocarbons at different temperatures.

INTRODUCTION

Gas chromatography is suitable for studying the relationship between retention parameters and solute properties, and we have previously carried out investigations on the behaviour of isoalkanes[1], benzene homologues and alkenes[2] on squalane.

In this paper, the relationship between gas chromatographic data and the molecular structure of naphthenes is discussed. This topic has been considered previously by other workers, but in a different manner. Schomburg and co-workers considered the behaviour of saturated and unsaturated alkyl-substituted cyclopentanes and methylcyclopentanes[3] and of other alkyl-branched and unsaturated cyclic hydrocarbons[4] on squalane based on the homomorphic factor. Loewenguth and Tourres[5] and Rijks and Cramers[6] published precise experimental data on the retention of cycloalkanes on squalane.

In this work we considered the relationship between vapour pressure, molecular volume and structure of hydrocarbons and the retention of C_5–C_9 cycloalkanes, a more detailed consideration of which was given in previous publications[1,7,8]. The investigation was carried out not only in order to predict the separation on the basis of the theoretical retention indices, but also with the purpose of calculating the vapour pressure of the cycloalkanes at different temperatures and their boiling points.

CALCULATION

The study was based on the theoretical assumption presented earlier[1] and the retention of cycloalkanes was considered in the same manner. The influence of the

different structural elements of naphthenes on their retention on squalane was studied. Several combinations of significant structural elements were examined in order to derive an equation that would lead to simple calculations. We succeeded in combining all of the elements in an equation of the type

$$SN = a_0 + R(b_1x_1 + b_2x_2) \quad (1)$$

where SN is the structural number, R is a qualitative characteristic with a value of zero when there is no substituent attached to the ring and a value of unity, when there are substituents, independent of their number. All of the elements related to the structures of the substituents are represented by a factor x_1, and those related to their positions by a factor x_2:

$$x_1 = n_{\text{ring}} + n_R + n_{CH_3} - n_L \quad (2)$$

$$x_2 = n_v + 2tr_{i,i}^{1,2;\,1,4} + cis_{i,i,i}^{1,2} - tr_{i,j}^{1,2} \quad (3)$$

where

n_{ring} = number of carbon atoms in the ring;
n_R = number of substituents R;
n_{CH_3} = number of the methyl groups attached to the straight chain of a substituent;
n_L = length of the straight chain of a substituent;
n_v = number of vacant positions in the ring;
$tr_{i,i}^{1,2;\,1,4}$ = number of 1,2- and 1,4-*trans*-dimethylcycloalkanes;
$cis_{i,i,i}^{1,2}$ = number of 1,2-*cis*-trimethylnaphthenes;
$tr_{i,j}^{1,2}$ = number of 1,2-*trans*-dialkylcycloalkanes with different substituents.

A matrix* from 30 cycloalkanes was constructed. The retention indices for calculations of SN according to eqn. 1 were taken from the literature[5,6]. The physicochemical properties of the cycloalkanes studied were calculated from their vapour pressures[9,10] and specific gravities[9,11]. After solving the matrix, the following values of the coefficients were obtained: $a_0 = -0.4867$, $b_1 = 1.3330$ and $b_2 = 1.0474$.

RESULTS AND DISCUSSION

The results illustrating the relationship between the retentions and structures of C_5–C_9 cycloalkanes are given in Table I. The values show that cyclopentane and cyclohexane have SN values of about zero, indicating that unsubstituted cycloalkanes are retained less strongly than their alkyl-substituted derivatives. The SN values of the other compounds calculated in the range 50–100° show that, like those of the isoalkanes, they are almost independent of temperature.

On increasing the length of the substituent, the difference in the entropy of solution of cycloalkanes seems to decrease, as follows from the values of Δ_1 which are connected with the entropy of cycloparaffins relative to *n*-paraffins. Branching of the substituent improved the retention, as was the case with the isoalkanes. The *trans*-isomers of 1,2-disubstituted naphthenes are more difficult to dissolve in the stationary phase used than *cis*-isomers, which was observed previously with olefins.

* A sum of data prepared for regression analysis.

TABLE I

DIFFERENCES Δ_1 BETWEEN I (RETENTION INDEX) AND PCI (PHYSICO-CHEMICAL INDEX) AND Δ_2 BETWEEN I AND I^{theor} (SUM OF PCI AND SN) FOR C_5–C_9 CYCLOALKANES

Hydrocarbon	Δ_1	Δ_2*
Cyclopentane	− 0.3	0.2
Methylcyclopentane	4.8	1.4
Ethylcyclopentane	4.4	0.4
n-Propylcyclopentane	3.1	0.4
Isopropylcyclopentane	7.4	1.2
Cyclohexane	− 0.2	0.7
Methylcyclohexane	7.9	0.4
Ethylcyclohexane	6.5	0.3
n-Propylcyclohexane	4.6	0.2
Isopropylcyclohexane	7.1	0.4
n-Butylcyclohexane	3.2	0.3
Isobutylcyclohexane	6.0	0.2
1,1-Dimethylcyclopentane	6.4	3.6
1-Methyl-1-ethylcyclopentane	9.7	0.7
1,1-Dimethylcyclohexane	13.6	0.8
1-*trans*-2-Dimethylcyclohexane	13.6	0.2
1-*cis*-2-Dimethylcyclohexane	11.9	0.2
1-*trans*-4-Dimethylcyclohexane	13.4	1.7
1-*cis*-4-Dimethylcyclohexane	10.2	0.6
1-*trans*-3-Dimethylcyclohexane	8.9	1.7
1-*cis*-3-Dimethylcyclohexane	9.3	1.3
1-Methyl-*cis*-2-ethylcyclopentane	7.6	0.4
1-Methyl-*trans*-2-ethylcyclopentane	6.2	0.7
1,1,1-Trimethylcyclopentane	8.9	0.6
1,1,1-Trimethylcyclohexane	12.4	1.8
1,1,2-Trimethylcyclopentane	11.4	2.1
1-*trans*-2-*cis*-4-Trimethylcyclopentane	8.4	2.0
1-*cis*-2-*trans*-4-Trimethylcyclopentane	10.2	1.2
1-*trans*-2-*cis*-3-Trimethylcyclopentane	11.9	0.5
1-*cis*-2-*cis*-3-Trimethylcyclopentane	13.8	0.3

* Variance of Δ_2: $s^2 = 0.97$.

Statistical analysis showed $F^{exp}_{(29,30)} = 1.57$ and $F^{0.05}_{tabular} = 1.87$. The value of 1.57 for the Fischer criterion ($F_{(f_1 f_2, 1-\alpha)}$; ref. 12) represents the relationship between variances for the 29 cycloalkanes in Table I (excluding 1,1-dimethylcyclopentane) and for the 30 cycloalkanes for which I^{exp} values have been published by different workers[4–6].

The accuracy achieved was examined by calculating the vapour pressures of different cycloalkanes and their temperature dependence and by calculating their boiling points. The principle can be demonstrated by considering *n*-propylcyclopentane. To calculate p^0, the following equation was used:

$$\log p_i^0 = \log \frac{p_z^0 \cdot V_{mol,z}}{V_{mol,i}} - \left(\frac{I^{theor} - SN}{100} - z \right) \log \frac{p_z^0 \cdot V_{mol,z}}{p_{z+1}^0 \cdot V_{mol,z+1}} \qquad (4)$$

where p_i^0 = vapour pressure of ith cycloparaffin; p_z^0 and p_{z+1}^0 = vapour pressures of *n*-paraffins with z and $z + 1$ carbon atoms, respectively; $V_{mol,i}$, $V_{mol,z}$ and $V_{mol,z+1}$

are the corresponding molecular volumes; I^{theor} = calculated theoretical index; and SN = calculated structural number.

Using literature values and our experimental data, we calculated p^0 for *n*-propylcyclopentane at several temperatures (Table II).

TABLE II

VAPOUR PRESSURE (p^0) OF *n*-PROPYLCYCLOPENTANE CALCULATED AT DIFFERENT TEMPERATURES

Temperature (°C)	I^{exp} *value*	*Reference*	$p^0_{calc.}$ *(mmHg)*
60	832.3	6	68.9
70	834.7	This work	103.0
80	836.3	6	151.8
90	838.5	This work	216.9
100	840.2	6	304.2

Values of the constants A, B and C of the Antoine equation were calculated from $p_{calc.}$ (Table II) and the following equation was obtained:

$$\log p^0_{n\text{-Prcp}} = 6.8328 - \frac{1348.9}{t + 210.14} \tag{5}$$

The vapour pressures over the range 20–200° were calculated and are compared in Table III with those given in the literature. The data show that the value of the constants A, B and C remain valid not only in the range 60–100°, which represents the limit of the available I values, but could be used in an extended range from 20 to 200° with satisfactory accuracy.

TABLE III

VAPOUR PRESSURE ($p°$) OF *n*-PROPYLCYCLOPENTANE AT DIFFERENT TEMPERATURES

Temperature (°C)	$p°$ *(mmHg)*		
	Literature value	*Calculated from A, B and C*	*Difference (mmHg)*
20	9.2	9.4	−0.2
40	27.3	27.5	−0.2
50	44.0	44.4	−0.4
80	151.9	151.8	−0.1
100	304.2	304.2	0.0
120	560.6	558.4	+2.2
180	2414	2373	+41 (1.7%)
200	3575	3498	+77 (2.2%)

The boiling points (t_b) of *n*-propylcyclopentane and other cycloalkanes could be calculated according to the equation

$$t_b = \frac{B}{A + \log 760} - C \tag{6}$$

The calculated and actual boiling points of different cycloalkanes are compared in Table IV.

TABLE IV

COMPARISON OF CALCULATED AND ACTUAL BOILING POINTS OF DIFFERENT CYCLOALKANES

Hydrocarbon	*Boiling point (°C)*		*Difference (°C)*
	Calculated	*Actual*	
Cyclopentane	49.0	49.26	0.26
1,1-Dimethylcyclopentane	87.66	87.84	0.18
1-*cis*-3-Dimethylcyclopentane	91.41	90.77	−0.64
1-Methyl-*trans*-2-ethylcyclopentane	121.36	121.20	−0.16
1-Methyl-1-ethylcyclopentane	119.84	121.52	1.68
Isopropylcyclopentane	126.62	126.40	−0.22
n-Propylcyclopentane	130.69	130.95	0.26
1-Methyl-*cis*-2-ethylcyclopentane	128.37	128.05	−0.32
1-Methyl-*trans*-2-ethylcyclopentane	146.2	146.3	0.1
sec-Butylcyclopentane	153.86	154.4	0.54
n-Butylcyclopentane	157.47	156.6	−0.9

The results obtained indicate the possibilities of utilizing I values both for identification purposes and for the calculation of p^0 at particular temperatures. The latter has the advantage of permitting the investigation of compounds in a mixture, because the value of I could easily be determined at different temperatures and is not influenced by the presence of other hydrocarbons.

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