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## QUALITATIVE GAS CHROMATOGRAPHIC ANALYSIS AND DETERMINATION OF SOLUTE PROPERTIES

### AN EXACT EQUATION FOR THE CALCULATION OF THE RETENTION INDICES OF ISOALKANES ON SQUALANE

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#### SUMMARY

Gas chromatography can be used to determine the properties of solutes in a mixture provided that an exact equation exists between the retention and the properties of interest. Several equations that permit easy laboratory calculations were studied and the accuracy of equations with a correlation coefficient above 0.85 was determined. The equation

$$I_t^{\text{theor}} = PCI_t - a + bn_G + c \cdot \frac{n_{\text{CH}_3} n_B}{n_L (n_0 - n_t)}$$

gives an average deviation from 0.0 to  $\pm 0.9$  index unit for the C<sub>6</sub>-C<sub>8</sub> isoalkanes separated on squalane at different temperatures.

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#### INTRODUCTION

The Kováts retention index system and instrumental methods are commonly used in qualitative gas chromatography (GC)<sup>1</sup>, the former technique is cheaper, while the latter is more reliable. When retention indices can be determined with an accuracy of  $\pm 0.1$  index unit (i.u.), the certainty of identifications based on them is improved. Under certain conditions, this accuracy is not difficult to achieve<sup>2-5</sup>. Identification is also facilitated by using the temperature dependence of the retention index ( $dI/dt$ ), as additional information<sup>6-9</sup>, but this procedure is time consuming.

Comparison of experimental with calculated retention indices also gives useful information, but the reliability of the results obtained depends on the accuracy of the method used. If the method is based on a suitable concept, GC can be used not only for analysis but also for the determination of some solute properties.

There are several methods for the calculation of  $I$ , such as those based on bond contributions (e.g., refs. 10 and 11), comparisons with the retentions and structures of compounds similar to the solute of interest (e.g., ref. 12), use of the homomorphic factor,

$H^{np}$  (refs. 13–15) or comparison of  $I_{exp}$  with an index calculated on the basis of  $I_{exp}$  and the structure of the compound being investigated (e.g., refs. 16–18). Although these methods are suitable for identification purposes<sup>15,19,20</sup>, they cannot be used for the calculation of solute properties from the retention indices. Because of its separation ability, GC could be utilized for this purpose with the same success as in analysis. In this respect, it is more important to find out an exact relationship between the retention indices and the physico-chemical characteristics of solutes. Attempts in this direction have been made previously (e.g., refs. 21–27).

This paper is intended to demonstrate an equation that is easy to use for the calculation of retention indices and sufficiently exact to give reliable identifications and to be used for the determination of some physico-chemical properties of solutes. The retention index ( $I^{theor}$ ) comprises two constituents: the physico-chemical index ( $PCI$ ), calculated on the basis of the vapour pressure and molecular volume of the solute and the corresponding  $n$ -alkanes<sup>24</sup>, and a correction (structural number,  $SN$ ), calculated on the basis of the solute structure. Using the separation of  $C_6$ – $C_{10}$  isoalkanes on squalane, the accuracy of some equations for the calculation of  $SN$  and  $I^{theor}$  has been determined.

## THEORETICAL

The theory of solutions used in GC should be regarded as a case of the general theory of solutions. Although the solute zone moves down the column in a relatively limited volume of stationary phase, the solution obtained could be considered to be infinitely dilute. Proceeding from this assumption, Herrington<sup>28</sup> determined the relative retention in GC by the equation

$$r_{1,2} = P_{2,1}^0 \cdot \gamma_{2,1} \quad (1)$$

The value of  $\gamma$  differs from unity as GC solutions cannot be ideal; even if the excess enthalpy of solution,  $H^m$ , is zero,  $S^m$  is non-zero as the molecular sizes of solutes and stationary phases differ significantly. There is little doubt that a phase that gives a maximal value of  $S_1^m - S_2^m$  is needed for the separation of closely related compounds. We shall now consider the separation in terms of  $S^m$ . From the equation

$$G^m = RT \ln \gamma \quad (2)$$

$\gamma$  can be expressed in two parts<sup>29</sup>:

$$\ln \gamma = \frac{H^m}{RT} - \frac{S^m}{R} = \ln \gamma_T + \ln \gamma_A \quad (3)$$

In regular solutions,  $S^m = 0$  and  $\ln \gamma = H^m/RT$ . A method for calculating the retention was given by Martire<sup>30</sup> and its application has been discussed<sup>31</sup> and studied experimentally<sup>32</sup>. In modern GC, however, one rarely encounters regular solutions, as they exist between molecules of very similar sizes, which indicates that the phase possesses a very high volatility. Regular solutions will therefore not be considered further.

In athermal solutions,  $H^m = 0$  and

$$\ln \gamma = -S^m/R \quad (4)$$

The value of  $S^m$  is determined in general by changes in the degrees of freedom in the different types of molecular motions. Let us assume that there is no change in the vibrational motions when only dispersion interactions occur. However, there are certain changes in the rotational degrees of freedom, especially when dissolving in phases with well packed molecules. Translation could be estimated by the so-called positional entropy,  $S_{pos}$ , by means of the following equation<sup>33</sup>:

$$S_{pos} = -R (\ln V_1/V_{ph} + 1 - V_1/V_{ph}) \quad (5)$$

where  $V_1$  and  $V_{ph}$  are the molecular volumes of solute 1 and the stationary phase.

By using eqn. 5, Hammers and De Ligny<sup>25,34</sup> derived an equation for calculating  $I_{p,v}$ . This equation, however, is not adequate in view of our aim, as a phase property ( $V_{ph}$ ) is included in the calculation. The determination of the molecular volume of the stationary phase is complicated because low-volatility, high-molecular-weight polymers that possess a certain polydispersity are used. Also, only a portion of the complete polymer molecule is assumed to take part in the retention of a low-molecular-weight solute<sup>35</sup>.

The following equation for relative separations on non-specific stationary phases has been suggested<sup>35</sup>:

$$r_{1,2} = p_{2,1}^0 \cdot V_{mol2,1} \quad (6)$$

A stationary phase could be considered to be non-specific provided that:

(1)  $H_2^m - H_1^m = 0$ .  $H^m$  is the excess enthalpy of solution of compounds 1 and 2. This might be assumed to apply when closely related compounds are separated.

(2)  $S_2^m - S_1^m = \Delta S^m$  consists mainly of  $\Delta S_{pos}$ . This is applicable to stationary phases with non-compact molecular packing. We then obtain

$$\Delta S^m = -R \left( \ln V_2/V_1 + \frac{V_1 - V_2}{V_{ph}} \right) \quad (7)$$

(3) The term  $\frac{V_1 - V_2}{V_{ph}}$  in eqn. 7 could be neglected, because  $V_1 - V_2 \ll V_{ph}$ .

Then,  $\Delta S^m = -R \ln V_{2,1}$  and  $\gamma_{2,1} = V_{2,1}$  (see eqn. 6).

Discrepancies between  $I_{exp}$  on different stationary phases and  $PCI$ , calculated from  $r_{1,2}$ , were examined and it was found that they are due to the neglect of the rotational contributions to  $\Delta S^m$ , rather than to the molecular volume of the phase. The more branched the isoalkane, the greater is the positive difference between  $I$  and  $PCI$ . Guidelines for the determination of the corrected  $PCI$  values of different hydrocarbons have been derived and a very good coincidence between  $I$  and  $PCI_{corr}$  was achieved<sup>36,37</sup>.

We give below some evidence on the important role of the rotational constituent of  $S^m$ , connecting the correction of  $PCI$  with selected structural elements of the corresponding isoalkanes by means of a correlative linear equation.

## RESULTS AND DISCUSSION

The accuracy of the methods for the calculation of retention indices given by Altenburg<sup>22</sup>, Martinov and Vigdergauz<sup>23</sup> and Hammers and De Ligny<sup>25</sup> should be

compared in terms of their own statistics.  $I_p$  calculated according to Bonastre and Grenier<sup>38</sup> and  $PCI$ <sup>24</sup> should also be included. The data for 16  $C_8$  isoalkanes were taken from or calculated according to these references and the results are given in Table I.

TABLE I

DISCREPANCIES BETWEEN  $I_{exp}$  VALUES AND  $I$  VALUES CALCULATED ACCORDING TO DIFFERENT INVESTIGATORS

No.	Hydrocarbon	Reference				
		22	23	38	25	24
1	2-Methylheptane	-2.4	1.2	- 3.5	- 0.9	1.3
2	3-Methylheptane	-1.9	1.3	- 0.3	1.6	2.5
3	4-Methylheptane	-4.2	2.5	- 1.2	0.7	2.3
4	3-Ethylhexane	-0.1	2.6	2.0	2.0	3.8
5	2,2-Dimethylhexane	2.4	2.2	- 7.2	- 2.2	3.0
6	2,3-Dimethylhexane	1.0	1.8	2.1	2.9	5.5
7	2,4-Dimethylhexane	2.2	2.3	- 4.2	0.9	4.0
8	2,5-Dimethylhexane	1.5	3.3	- 7.5	- 1.4	1.9
9	3,3-Dimethylhexane	-1.9	1.5	1.3	4.2	7.0
10	3,4-Dimethylhexane	-1.4	0.3	5.8	-	7.2
11	2-Methyl-3-ethylpentane	3.6	-1.3	4.8	4.7	7.1
12	3-Methyl-3-ethylpentane	-2.2	2.0	12.2	-	12.3
13	2,2,3-Trimethylpentane	1.7	-0.3	4.2	6.1	9.9
14	2,2,4-Trimethylpentane	0.9	-0.8	- 7.2	1.8	7.2
15	2,3,3-Trimethylpentane	0.4	-1.8	11.2	11.2	13.2
16	2,3,4-Trimethylpentane	2.7	0.0	5.4	-	8.9
Average deviation, $\Delta$		0.15	1.05	1.10	2.45	6.05
Dispersion, $s^2$		5.0	2.35	37.10	12.72	13.60
Standard deviation, $\sigma$		$\pm 2.2$	$\pm 1.5$	$\pm 6.1$	$\pm 3.6$	$\pm 3.7$

The data in the first two columns of values are based on the dependence of  $I$  on the molecular weight, density and structure. The equations used, however, were different in each instance. The data in the first column were obtained from  $I$  values calculated according to the equation<sup>22</sup>

$$I = -1273.2 + 22.307 Md_4^{20} + 136 K_R^2 \quad (8)$$

while the data in the second column were obtained from  $I$  values calculated according to the equation<sup>23</sup>

$$I = 800 - 4.5 (125.655 - t_b) + 22.5 (2.0252 - K_R^2) \quad (9)$$

The constants have different values or even the equation is changed when the corresponding  $n$ -alkanes are considered<sup>23</sup>. The value of the calculated retention index does not depend on temperature, which results in a significant difference between the dispersions at the 90% level: experimentally,  $F_{(16,16)}^{0.1} = \frac{s_{(22)}^2}{s_{(23)}^2} = 2.16$ , while the tabular  $F_{(16,16)} = 1.94$ .

The data in the last three columns were obtained from an  $I_{\text{calc}}$  value in which a parameter dependent on the temperature is involved, viz., the vapour pressure of the solutes. The discrepancies between  $I_p$  and  $PCI$  show that the dispersion improved significantly after including the molecular volume of the solutes in the calculation. Neither  $\Delta$  nor  $\sigma$  is minimized sufficiently when the molecular volume of the stationary phase is included in the calculation. In addition, the dispersions in the last two columns are equal at the 90% level: experimentally,  $F_{(16,13)} = 1.07$ , while the tabular  $F_{(16,13)} = 2.05$ .

All of the differences in the last column are positive, whereas in the other columns they are both positive and negative. Evidently a systematic correction to the  $PCI$  is necessary. If such a correction could be calculated and its dispersion were less than 1 i.u., the new theoretical retention index could be used successfully for the determination of solute properties. It is also evident that this correction should not be connected with the molecular volume of the stationary phase, especially when working with apolar stationary phases. The data in Table I show that the retention could not be expressed entirely in terms of the structure or the vapour pressure only.

In a previous paper<sup>9</sup>, it was shown that the dependence of the  $PCI$  on temperature corresponds to  $dI_{\text{exp}}/dt$ . Over a temperature range of 40°, the maximum error observed for the 31 isoalkanes studied is 1 i.u. Hence a temperature-dependent variation is introduced into the new theoretical retention index when the  $PCI$  is involved as one of its components. The value of the second constituent of this retention index is connected with a loss of rotational degrees of freedom due to the solution in the stationary phase. In other words, the differences between  $I_{\text{exp}}$  and  $PCI - \Delta$  are connected with the rotational constituent of  $S^m$ . This connection is expressed by means of the "structural number"  $SN$ , consisting of the contributions of different structural elements of the solute.

Several structural elements of  $C_6$ - $C_{10}$  isoalkanes were selected and treated. The data used in the calculations are given in Table II. The values of  $I_{\text{exp}}$  were taken mainly from ref. 39. The  $PCI$  values were calculated at 70°. The number of Gosh conformations ( $n_G$ ) was taken from ref. 22. The numbers of methyl groups ( $n_{\text{CH}_3}$ ), butane chains ( $n_B$ ), tertiary carbon atoms ( $n_t$ ), the total number of carbon atoms ( $n_0$ ) and the length of the straight chain ( $n_L$ ) were derived from the structures of the isoalkanes.

After studying the relationship between the structural elements and  $\Delta$ , the following combinations for calculation of the structural number,  $SN$ , are suggested:

$$X_1 = n_G \quad (10)$$

$$X_2 = \frac{n_B \cdot n_{\text{CH}_3}}{n_L} \quad (11)$$

$$X_3 = \frac{n_B + n_{\text{CH}_3}}{n_L + n_0 - n_t} \quad (12)$$

$$X_4 = \frac{n_B \cdot n_{\text{CH}_3}}{n_L (n_0 - n_t)} \quad (12a)$$

If the number of Gosh conformations,  $n_G$ , only is taken into account, the correlation coefficient calculated for the  $C_6$ - $C_8$  isoalkanes is 0.96. We assume that the greater

TABLE II  
INITIAL DATA FOR CALCULATIONS

No.	Hydrocarbon	$I_{exp}^{70}$	$PCI^{70}$	$n_G$	$n_B$	$n_{CH_3}$	$n_0$	$n_L$	$n_r$
1	2,2-Dimethylbutane	538.5	532.7	2	3	4	6	4	1
2	2,3-Dimethylbutane	568.9	562.9	2	4	4	6	4	0
3	2-Methylpentane	570.0	568.9	1	3	3	6	5	0
4	3-Methylpentane	585.1	581.5	2	4	3	6	5	0
5	2,2-Dimethylpentane	627.0	623.1	2	4	4	7	5	1
6	2,3-Dimethylpentane	673.4	666.9	3	6	4	7	5	0
7	2,4-Dimethylpentane	630.5	628.0	2	4	4	7	5	0
8	2,2,3-Trimethylbutane	642.6	631.4	4	6	5	7	4	1
9	3,3-Dimethylpentane	661.5	651.4	4	6	4	7	5	1
10	2-Methylhexane	667.0	665.0	1	4	3	7	6	0
11	3-Methylhexane	676.9	674.0	2	5	3	7	6	0
12	3-Ethylpentane	687.2	682.4	3	6	3	7	5	0
13	2,2,4-Trimethylpentane	692.0	684.8	3	5	5	8	5	1
14	2,2-Dimethylhexane	720.5	717.5	2	5	4	8	6	1
15	2,4-Dimethylhexane	733.0	729.0	3	6	4	8	6	0
16	2,5-Dimethylhexane	729.0	727.1	2	5	4	8	6	0
17	2,2,3-Trimethylpentane	740.2	730.3	5	8	5	8	5	1
18	3,3-Dimethylhexane	745.9	738.9	4	7	4	8	6	1
19	2,3,4-Trimethylpentane	755.1	746.2	4	8	5	8	5	0
20	2,3,3-Trimethylpentane	763.4	750.2	6	9	5	8	5	1
21	2,3-Dimethylhexane	761.5	756.0	3	7	4	8	6	0
22	2-Methyl-3-ethylpentane	763.5	756.4	4	8	4	8	5	0
23	2-Methylheptane	765.2	764.0	1	5	3	8	7	0
24	4-Methylheptane	767.7	765.4	2	6	3	8	7	0
25	3,4-Dimethylhexane	772.6	765.4	4	8	4	8	6	0
26	3-Methylheptane	772.9	770.4	2	6	3	8	7	0
27	3-Ethylhexane	773.4	769.6	3	7	3	8	6	0
28	3-Methyl-3-ethylpentane	777.5	765.2	5	9	4	8	5	1

is  $n_G$ , the more easily are the solute molecules incorporated in the net of the stationary phase molecules.

The rotation of the whole molecule also has an influence on the retention. This influence can be expressed by including  $n_{CH_3}$  and  $n_L$  in eqn. 11; the greater is  $n_{CH_3}$  and the smaller is  $n_L$ , the more compact are the solute molecules and hence the smaller is the restriction of its rotation in the stationary phase. The correlation coefficient obtained for  $X_2$  is 0.94.

As a higher accuracy is achieved,  $n_0$  and  $n_r$  are introduced into eqns. 12 and 12a. The structural number,  $SN$ , is calculated from linear equations such as

$$SN = a + b \cdot X_1$$

or

$$SN = a + b \cdot X_1 + c \cdot X_2$$

where the values of the constants  $a$ ,  $b$  and  $c$  are determined by the least-squares method

using the data for 28  $C_6$ - $C_8$  isoalkanes. The following equations that have given satisfactory results were studied further:

$$SN = 2.46X_1 - 1.5 \quad (13)$$

$$SN = 18.47X_3 - 8.39 \quad (14)$$

$$SN = 11.41X_4 - 1.5 \quad (15)$$

$$SN = 1.36X_1 + 0.755X_2 - 1.61 \quad (16)$$

$$SN = 0.90X_1 + 7.735X_4 - 1.82 \quad (17)$$

The discrepancies between  $I$  and  $I^{\text{theor}}$  were determined (Table III). All of the statistical values were more satisfactory than those in Table I.

TABLE III

DIFFERENCES ( $\Delta$ ) BETWEEN  $I_{\text{exp}}$  AND RETENTIONS CALCULATED AT 70° ACCORDING TO EQNS. 13-17

No.	Hydrocarbon	$\Delta$ (i.u.)				
		Eqn. 13	Eqn. 14	Eqn. 15	Eqn. 16	Eqn. 17
1	2,2-Dimethylbutane	2.40	0.45	2.40	1.15	-0.20
2	2,3-Dimethylbutane	2.60	-0.10	1.90	0.85	-0.40
3	2-Methylpentane	0.15	-0.80	0.00	-0.30	-0.60
4	3-Methylpentane	0.20	0.55	0.70	0.50	0.25
5	2,2-Dimethylpentane	0.45	-0.65	0.35	-0.20	-1.15
6	2,4-Dimethylpentane	-0.90	-1.20	-1.00	-1.00	-1.40
7	2,2,3-Trimethylbutane	2.85	-1.55	1.70	-0.25	-0.75
8	3,3-Dimethylpentane	1.75	2.45	2.65	2.10	1.70
9	2-Methylhexane	1.05	0.25	0.75	0.70	0.45
10	2,3-Dimethylpentane	0.60	0.15	0.40	0.30	-0.50
11	3-Methylhexane	-0.50	0.30	-0.10	0.15	-0.05
12	3-Ethylpentane	-1.10	0.45	-0.40	-0.05	-0.65
13	2,2,4-Trimethylpentane	-1.30	0.55	0.95	0.80	0.20
14	2,2-Dimethylhexane	-0.40	-0.90	-0.60	-0.65	-1.40
15	2,5-Dimethylhexane	-1.50	-1.35	-1.70	-1.30	-1.60
16	2,4-Dimethylhexane	-1.90	-0.20	-1.50	-0.75	-0.80
17	2,2,3-Trimethylpentane	-1.80	-1.60	-1.30	-1.65	-1.70
18	3,3-Dimethylhexane	-1.35	0.90	-0.35	0.05	-0.25
19	2,3,4-Trimethylpentane	0.55	-1.00	-0.95	-0.65	2.70
20	2,3,3-Trimethylpentane	-0.05	0.00	-0.15	-0.35	0.05
21	2,3-Dimethylhexane	-0.40	0.25	-0.50	0.10	0.65
22	2-Methyl-3-ethylpentane	-1.25	-0.50	-1.55	-0.90	-1.60
23	2-Methylheptane	0.25	-0.35	0.00	0.05	-0.25
24	4-Methylheptane	-1.10	0.10	-0.75	-0.20	-0.40
25	3,4-Dimethylhexane	-1.15	1.20	-0.65	0.25	-0.25
26	3-Methylheptane	-0.95	0.30	-0.55	0.00	-0.20
27	3-Ethylhexane	-2.10	0.30	-1.30	-0.45	-1.00
28	3-Methyl-3-ethylpentane	1.50	2.05	1.70	1.65	-0.70
Average deviation, $\Delta$		0.03	-0.60	0.00	0.01	0.00
Dispersion, $s^2$		1.96	0.69	0.96	1.47	0.71
Standard deviation, $\sigma$		$\pm 1.4$	$\pm 0.85$	$\pm 1.0$	$\pm 1.2$	$\pm 0.85$

The preliminary determination of  $n_G$ , necessary for use in eqns. 13, 16 and 17, might be unnecessary when eqns. 14 and 15 are used. If  $I^{\text{theor}}$  is calculated in order to confirm an identification, the probable identity of the compound must have been assumed. If the proposed equations are used as a prediction step in the separation, the structure of the compound of interest will be known in advance. If  $I_{\text{exp}}$  is used to calculate the vapour pressure,  $p^0 - f(t)$  or  $V_{\text{mol}}(d_4^t)$ , the compounds of interest are also known in advance. Obviously there are no difficulties when  $n_o$ ,  $n_i$ ,  $n_L$ ,  $n_B$  and  $n_{\text{CH}_3}$  are to be determined.

The accuracy of the method had also to be demonstrated for separations at other temperatures and of higher isoalkanes. These calculations were carried out according to eqn. 14, because it has a greater average deviation. For example,  $I^{\text{theor}}$  values at 100° were calculated and compared with  $I_{\text{exp}}$  (Table IV). Although the dispersion has proved to be higher ( $s^2$  at 100° is 0.89, while at 70° it is 0.69), a comparison by means of the  $F$  factor did not show any significant difference at the 90% level.

$I^{\text{theor}}$  values for  $C_9$  and  $C_{10}$  isoalkanes were also calculated. The standard deviation for  $C_9$  isoalkanes was  $\pm 1.7$  i.u., while that for the  $C_{10}$  isoalkanes was above 5

TABLE IV

DIFFERENCES ( $\Delta$ ) BETWEEN  $I_{\text{exp}}$  AND RETENTIONS CALCULATED AT 100° ACCORDING TO EQN. 14

No.	Hydrocarbon	$I_{\text{exp}}$	PCI	SN	$I_{\text{calc}}$	$\Delta$
1	2,2-Dimethylbutane	541.0	534.4	5.45	539.85	1.15
2	2,3-Dimethylbutane	571.2	564.9	5.85	571.75	-0.55
3	2-Methylpentane	570.6	569.1	1.25	570.35	0.25
4	3-Methylpentane	586.4	582.65	2.9	585.55	0.85
5	2,2-Dimethylpentane	628.9	623.8	4.55	628.35	0.45
6	2,4-Dimethylpentane	631.5	628.2	3.45	631.65	-0.15
7	2,2,3-Trimethylbutane	646.9	635.0	11.2	646.2	0.70
8	3,3-Dimethylpentane	665.5	654.7	7.8	662.5	3.0
9	2-Methylhexane	667.5	666.0	1.15	667.15	0.35
10	2,3-Dimethylpentane	675.9	668.7	6.45	675.15	0.75
11	3-Methylhexane	677.9	675.0	2.55	677.55	0.35
12	3-Ethylpentane	688.9	682.85	4.95	687.8	1.1
13	2,2,4-Trimethylpentane	695.3	686.85	6.45	693.35	1.95
14	2,2-Dimethylhexane	722.1	718.1	3.9	722.0	0.1
15	2,5-Dimethylhexane	729.9	727.4	3.0	730.4	-0.5
16	2,4-Dimethylhexane	734.5	728.45	4.3	732.75	1.75
17	2,2,3-Trimethylpentane	744.8	733.9	10.9	744.8	0.0
18	3,3-Dimethylhexane	749.5	741.6	6.7	748.3	1.2
19	2,3,4-Trimethylpentane	759.2	749.6	10.9	760.5	-1.3
20	2,3,3-Tri-methylpentane	769.5	755.6	12.4	768.0	1.5
21	2,3-Dimethylhexane	761.8	758.05	5.6	763.65	1.85
22	2-Methyl-3-ethylpentane	766.7	758.95	8.0	766.95	-0.25
23	2-Methylheptane	765.6	764.35	1.05	765.4	0.2
24	4-Methylheptane	768.5	765.8	2.25	768.05	0.45
25	3,4-Dimethylhexane	775.6	767.8	6.85	774.7	0.9
26	3-Methylheptane	773.8	771.35	2.25	773.6	0.2
27	3-Ethylhexane	774.9	771.0	4.3	775.3	-0.4
28	3-Methyl-3-ethylpentane	783.2	770.15	10.9	781.05	2.15



i.u. When calculating the new constants  $a$  and  $b$  for the 900–1000 i.u. range, eqn. 18 is obtained:

$$SN_{9-10} = 19.02X_3 - 8.38 \quad (18)$$

which decreased the discrepancies between  $I^{\text{theor}}$  and  $I_{\text{exp}}$ . The lack of sufficient data for  $C_{10}$  isoalkanes obtained according to the recommendations in refs. 2–5 can be offered as a reason for the higher values of  $\Delta$  in this range.

When applying eqns. 14 and 18, the following accuracy in the calculation of  $I^{\text{theor}}$  at different temperatures within the range 500–1000 i.u. was obtained:

500–600 i.u.	$s^2 = 0.3$ ; $\sigma = \pm 0.5$ i.u.
600–700 i.u.	$s^2 = 1.1$ ; $\sigma = \pm 1$ i.u.
700–800 i.u.	$s^2 = 0.65$ ; $\sigma = \pm 0.8$ i.u.
800–900 i.u.	$s^2 = 2.85$ ; $\sigma = \pm 1.7$ i.u.
900–1000 i.u.	$s^2 = 10$ ; $\sigma = \pm 3$ i.u.

The accuracy achieved in the calculation of  $I^{\text{theor}}$  makes it a useful source of information when an identification or a prediction of a separation in qualitative GC is required. On the other hand, the correct calculation of  $p^0$  and  $dp/dt$  becomes possible when  $I^{\text{theor}}$  is replaced with  $I_{\text{exp}}$ .

#### LIST OF SYMBOLS

$a, b, c$	= empirical constants
$d_t^i$	= density at $t$ °C
$F_{(t_1, t_2)}^{0,1}$	= Fisher criterion (statistics)
$G^m$	= excess free energy of solution
$H^m$	= excess enthalpy of solution
$I_{\text{calc}}$	= calculated retention index
$I_{\text{exp}}$	= Kováts retention index
$I_{p, V}$	= retention index calculated from $p^0$ , $V_{\text{mol}}$ and $V_{\text{ph}}$
$I_p$	= retention index calculated from $p^0$
$I^{\text{theor}}$	= sum of $PCI$ and $SN$
$M$	= molecular weight
$p_{2/1}^0$	= $p_2^0/p_1^0$ , where $p^0$ is the vapour pressure of the solute
$R$	= gas constant
$r_{1,2}$	= relative retention of solutes 1 and 2
$S^m$	= excess entropy of solution
$S_{\text{pos}}$	= positional entropy
$t_{\text{b.p.}}$	= boiling point
$V_{\text{mol}, 1,2}$	= $V_{\text{mol}, 2}/V_{\text{mol}, 1}$ , where $V_{\text{mol}}$ is the molar volume of the solute
$V_{\text{ph}}$	= molar volume of the phase

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