Retention Index, Connectivity Index and Van der Waals' Volume of Alkanes (GLC)

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Key Words

Gas chromatography
Retention index
Connectivity index
Van der Waals' volume
Alkanes

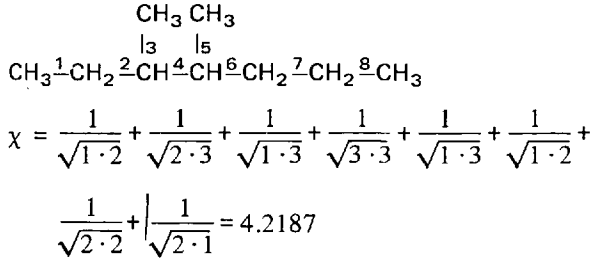
Summary

The relationships between retention index and Van der Waals' volume and between retention index and connectivity index have been studied for 58 different alkanes (C_1 – C_9) on squalane. The correlation coefficient for the former is higher than for the latter. From these equations a linear relationship between Van der Waals' volume and connectivity index is obtained which indicates that the two parameters are equivalent. A simple method for calculating the Van der Waals' volume of alkanes is proposed.

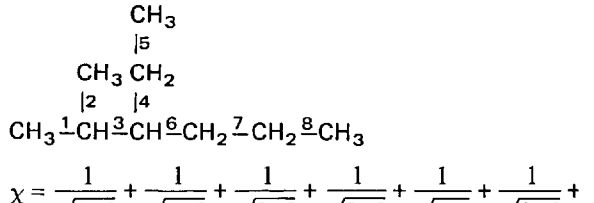
Introduction

It is well-known that branched organic compounds produce a decrease in chromatographic retention compared with linear compunds of the same relative molecular mass. Retention index (I) can thus be used as an experimental measure of the extent of molecular branching as proposed by Kovats [1]. For this reason it would be very useful to have an empirical molecular parameter correlated with the retention index which could be used as a theoretical measure of molecular branching. Along these lines, Randic [2] has proposed a theoretical method based on the calculation of a so-called branching or connectivity index (χ) for alkanes.

Examples of the calculation of this index are:



$$\chi = \frac{1}{\sqrt{1\cdot2}} + \frac{1}{\sqrt{2\cdot3}} + \frac{1}{\sqrt{1\cdot3}} + \frac{1}{\sqrt{3\cdot3}} + \frac{1}{\sqrt{1\cdot3}} + \frac{1}{\sqrt{1\cdot2}} + \frac{1}{\sqrt{2\cdot2}} + \left|\frac{1}{\sqrt{2\cdot1}}\right| = 4.2187$$



$$\chi = \frac{1}{\sqrt{1\cdot3}} + \frac{1}{\sqrt{1\cdot3}} + \frac{1}{\sqrt{3\cdot3}} + \frac{1}{\sqrt{3\cdot3}} + \frac{1}{\sqrt{2\cdot1}} + \frac{1}{\sqrt{3\cdot2}} + \frac{1}{\sqrt{2\cdot2}} + \frac{1}{\sqrt{2\cdot1}} = 4.2187$$

Several authors have studied the application of χ to different organic compounds such as pyrazine carbothiamide systems [3], complex cyclic structures [4], aromatic hydrocarbons [5], fatty acid methyl esters [6] and alkanes [7]. In general, equations of the type

$$I = a\chi + b \qquad (1)$$

are obtained in these papers.

The connectivity index is a non-dimensional parameter, however, and is incapble of differentiating between isomers in all cases. For example:

3,4	Dimethyl heptane	$\chi = 4.2187$	I = 858.4*
2	Methyl 3 ethyl hexane	$\chi = 4.2187$	I = 843.7
2,4	Dimethyl heptane	$\chi = 4.1639$	I = 821.5
2,5	Dimethyl heptane	$\chi = 4.1639$	I = 832.9

(* I values were determined on squalane at 50 °C)

A given value of χ may correspond to different retention indices.

In other cases, correlations between χ and I are anomalous. For example:

Heptane	$\chi = 3.4142$	I = 700
2,2,3,3 Tetramethyl butane	$\chi = 3.2500$	I = 726.1
3,5 Dimethyl octane	$\chi = 4.2019$	I = 833.7
2,2,3 Trimethyl hexane	$\chi = 4.0040$	I = 840

That is to say, higher χ values may correspond to compounds with lower I values.

In a previous paper [8] the authors studied the correlation between I and Van der Waals' volume (V_w) for different homologous series (n-alkanes, aldehydes, ketones and esters).

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Examples of calculation of V_w following the Bondi method [9] are:

$CH_3-(CH_2)_6-CH_3$

$V_w = 2V_{w(-CH_3)} + 6V_{w(-CH_2-)} = 2 \cdot 13.67 + 6 \cdot 10.23 = 88.72$

$CH_3-CH(CH_3)-CH(CH_3)-CH_2-CH_2-CH_3$

$V_w = 4V_{w(-CH_3)} + 2V_{w(-CH_2-)} + 2V_{w(-CH-)} =$
$= 4 \cdot 13.67 + 2 \cdot 10.23 + 2 \cdot 6.78 = 88.70$

It was demonstrated that V_w, a steric parameter, is the principal factor affecting chromatographic retention and that the significance of electrostatic parameters are limited in their influence to the first member in each homologous series. Equations of the type

$$I = a V_w + b \qquad (2)$$

were obtained.

The applicability of these equations is reduced, however, because the Bondi method for calculating V_w does not differentiate among isomers. For example:

Octane	$V_w = 88.72$ cm^3 mol^{-1}	I=800
2,3 Dimethyl hexane	$V_w = 88.70$ cm^3 mol^{-1}	I=772.9
3 Ethyl hexane	$V_w = 88.71$ cm^3 mol^{-1}	I=760.4

In this paper, the correlation between χ and V_w is studied by means of Eq. (1) and (2). A method for calculating V_w capable of differentiating among all alkane isomers is also examined.

Results and Discussion

Fig. 1 shows the straight lines I versus χ and I versus V_w for n-alkanes. The equations of these lines are:

$$I = 7.623 + 202.669\chi \qquad (3)$$

$N = 8 \quad R = 0.9998 \quad s = 5.44 \quad F = 14168.68$

$$I = -67.205 + 9.775\, V_w \qquad (4)$$

$N = 9 \quad R = 1.0000 \quad s = 0.03 \quad F = 7.06 \cdot 10^5$

where N = number of compounds employed; R = correlation coefficient; s = standard deviation; F = experimental value of Snedecor test.

As can be observed, the first two members, methane and ethane, are included in eq. (4), which indicates that this equation better represents the n-alkanes than eq. (3).

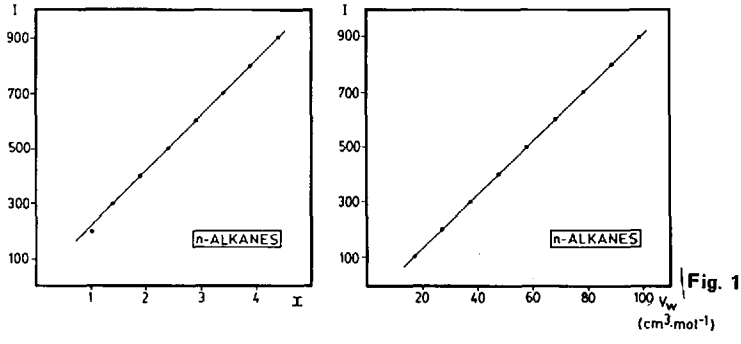


Fig. 1

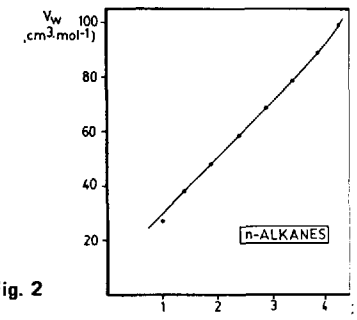


Fig. 2

From (3) and (4), the equation

$$V_w = 20.756\chi + 7.611 \qquad (5)$$

$N = 8 \quad R = 0.9996 \quad s = 0.54 \quad F = 14917.53$

can be obtained. This equation shows these magnitudes to be correlated and connectivity to be another way of expressing Van der Waals' volume. V_w has a concrete physical significance and units (the volume occupied by a molecule which is impenetrable by other molecules [9], cm^3 mol^{-1}), while the connectivity index is non-dimensional.

Plots of V_w versus χ appear in Fig. 2 Eq. (3), (4), and (5) are independent of the stationary phase because for n-alkanes I is 100 X n for all phases (n is the number of carbon atoms) and χ and V_w are molecular parameters.

By plotting I for squalane at 50 °C (Table I) versus χ for linear and branching alkanes, a straight line is obtained as can be seen in Fig. 3. This straight line is similar to the corresponding one for n-alkanes. If we then employ eq. (3) for all alkanes the statistics and correlation coefficient are satisfactory:

$$I = 7.623 + 202.669\chi \qquad (3')$$

$N = 57 \quad R = 0.9867 \quad s = 25.03 \quad F = 4245.51$

For this reason the equation can be applied to all alkanes on squalane.

The most satisfactory straight line is obtained by linear regression, resulting in the following equation:

$$I = 31.315 + 195.868\chi \qquad (6)$$

$N = 57 \quad R = 0.9937 \quad s = 17.30 \quad F = 4294.58$

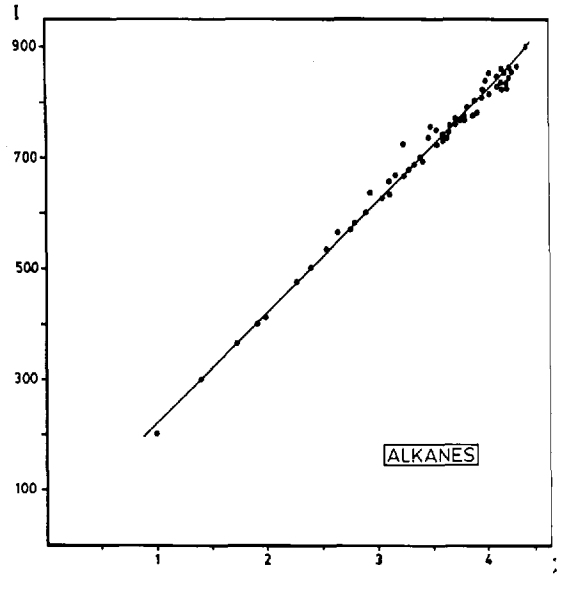


Fig. 3

Table I. Retention indices, Van der Waals' volumes and connectivity indices for alkanes

Compound	I*	V_w(cm³ mol⁻¹)	χ
Methane	100.0	17.10	–
Ethane	200.0	27.34	1.0000
Propane	300.0	37.57	1.4142
2-M-propane	365.7	44.85	1.7321
Butane	400.0	47.80	1.9142
2,2-DM-propane	412.6	50.80	2.0000
2-M-butane	474.9	55.08	2.2701
Pentane	500.0	58.03	2.4142
2,2-DM-butane	536.6	61.03	2.5607
2,3-DM-butane	567.6	64.02	2.6425
2-M-pentane	569.5	65.31	2.7700
3-M-pentane	584.0	66.10	2.8082
Hexane	600.0	68.26	2.9142
2,2-DM-pentane	625.9	71.26	3.0607
2,4-DM-pentane	629.9	71.00	3.1259
2,2,3-TM-butane	639.8	71.48	2.9432
3,3-DM-pentane	658.9	73.39	3.1213
2-M-hexane	666.9	75.54	3.2700
2,3-DM-pentane	671.7	75.04	3.1807
3-M-hexane	676.2	76.33	3.3081
3-E-pentane	685.9	76.10	3.3461
2,2,4-TM-pentane	690.1	76.95	3.4165
Heptane	700.0	78.49	3.4142
2,2-DM-hexane	719.7	81.49	3.5607
2,2,3,3-TeM-butane	726.1	81.06	3.2500
2,5-DM-hexane	728.5	81.50	3.6259
2,4-DM-hexane	732.1	82.02	3.6639
2,2,3-TM-pentane	737.3	82.50	3.6259
3,3-DM-hexane	743.7	83.62	3.6213
2,3,4-TM-pentane	752.5	83.98	3.5534
2,3,3-TM-pentane	759.8	83.84	3.5040
2,3-DM-hexane	760.4	85.27	3.6807
2-M-3-E-pentane	761.6	85.04	3.7188
2-M-heptane	764.8	85.77	3.7701
4-M-heptane	767.5	86.56	3.8081
3,4-DM-hexane	770.9	86.06	3.7188
3-M-heptane	772.2	86.56	3.8081
3-E-hexane	772.9	86.33	3.8510
2,2,5-TM-hexane	776.7	87.45	3.9165
2,2,4-TM-hexane	789.5	87.97	3.8248
Octane	800.0	88.72	3.9142
2,4,4-TM-hexane	808.2	89.31	3.9772
2,3,5-TM-hexane	812.4	90.96	4.0367
2,4-DM-heptane	821.5	92.25	4.1639
2,2,3-TM-hexane	821.9	92.73	3.9814
2-M-4-E-hexane	824.3	92.02	4.2019
4,4-DM-heptane	827.6	93.85	4.1213
2,5-DM-heptane	832.9	92.52	4.1639
3,5-DM-heptane	833.7	93.04	4.2019
2,3,3-TM-hexane	840.0	94.07	4.0040
2-M-3-E-hexane	843.7	95.27	4.2187
2,3,4-TM-hexane	846.6	95.00	4.0914
3,3,4-TM-hexane	853.1	94.86	4.0402
3-M-3-E-hexane	853.5	96.23	4.1820
3-M-4-E-hexane	854.8	96.06	4.2567
3,4-DM-heptane	858.4	96.29	4.2187
4-M-octane	863.1	96.79	4.3081
Nonane	900.0	98.95	4.4142

(*) – squalane at 50 °C [10, 11]
Nomenclature: M = methyl; E = ethyl; DM = dimethyl; TM = trimethyl; TeM = tetramethyl.

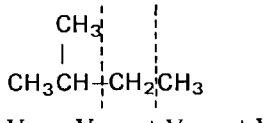
Squalane was chosen as the stationary phase because its polarity is low (zero), making it possible to avoid electrostatic interaction between solute and stationary phase. For this reason eq. (3) can represent the n-alkanes and the branching alkanes simultaneously. Also, this equation is applicable over a wide range of temperatures under the usual experimental conditions in GLC (25–200 °C) because the corresponding variation of I is very small and does not significantly affect the statistics or correlation coefficient of eq. (3). The I values corresponding to this temperature range have been calculated from the ΔI/10 °C values published [10].

As χ and V_w are correlated (eq. (5)) and eq. (3) represents all alkanes, an equation similar to eq. (4) (I versus V_w) would also represent all the alkanes. This makes desirable an easy method for calculating Van der Waals' volume which differentiates between isomeric alkanes and this is not posible by Bondi's method. For this reason we propose here a method for calculating V_w based on group contribution.

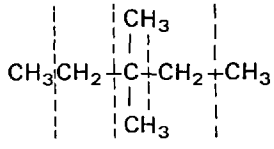
Calculation of V_w

It is possible to obtain V_w for each alkane from the connectivity and by applyng eq. (5). From the V_w values so calculated the volumes of groups have been included in Table II.

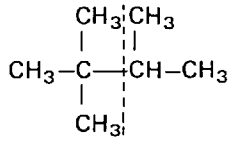
The volumes of groups listed in Table II facilitate calculation of V_w of any alkane. Examples of these calculations are: ($V_{w(x)}$ is the Van der Waals' volume corresponding to the group number x indicated in Table II)



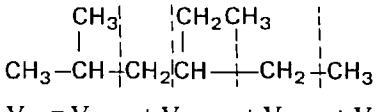
$$V_w = V_{w(5)} + V_{w(3)} + V_{w(2)} =$$
$$= 31.18 + 10.23 + 13.67 = 55.08 \text{ cm}^3 \text{ mol}^{-1}$$



$$V_w = 2V_{w(2)} + 2V_{w(3)} + V_{w(9)} =$$
$$= 2 \cdot 13.67 + 2 \cdot 10.23 + 25.59 = 73.39$$



$$V_w = V_{w(6)} + V_{w(5)} + V_{w(a)} = 71.48$$



$$V_w = V_{w(5)} + V_{w(11)} + V_{w(8)} + V_{w(3)} + V_{w(2)} = 92.02$$

This method provides for differentiation between isomers in some cases where the connectivity index does not. For example:

3,4 Dimethyl heptane $\chi = 4.2187$ $V_w = 96.29$ I = 858.4
2 Methyl 3 ethyl hexane $\chi = 4.2187$ $V_w = 95.27$ I = 843.7

Table II. Group contributions to Van der Waals' volume

	Group	$V_w(cm^3mol^{-1})$
1	CH_4	17.10*
2	CH_3-	13.67*
3	$-CH_2-$	10.23*
4	$-\overset{\vert}{C}H-$	6.78*
5	$CH_3-\overset{\vert}{C}H-CH_3$	31.18
6	$CH_3-\overset{\vert}{\underset{\vert}{C}}(CH_3)-CH_3$	37.13
7	$-\overset{\vert}{C}H(CH_3)-$	18.30
8	$-\overset{\vert}{C}H(CH_2-CH_3)-$	28.30
9	$-\overset{\vert}{\underset{\vert}{C}}(CH_3)_2-$	25.59
10	$-\overset{\vert}{\underset{\vert}{C}}(CH_2-CH_3)(CH_3)-$	38.20
11	$R-CH_2-R^\circ$	8.64
12	$R-CH_2-CH_2-R^\circ$	19.14
	Corrections	
a	C(4) together C(3)	+ 3.17
b	C(3) togehter C(3)	+ 1.66
c	C(4) together C(4)	+ 6.80

(°) – R = C(3) or C(4), where C(4) = quaternary carbon atom $(-\overset{\vert}{\underset{\vert}{C}}-)$ and C(3) = tertiary carbon atom $(-\overset{\vert}{C}H-)$

(*) – Calculated by Bondi [9]

The plot I vs. V_w calculated by this proposed method is shown in Fig. 4.

Also, for the same reason already indicated for I versus χ (eq. (3')) eq. (4') represents all alkanes. The statistics and correlation coefficient are:

$$I = -67.205 + 9.775\ V_w \qquad (4')$$

$$N = 58 \quad R = 0.9978 \quad s = 11.51 \quad F = 25567.99$$

Eq. (4') is better than (3') which could indicate that V_w represents more exactly the chromatographic retention of

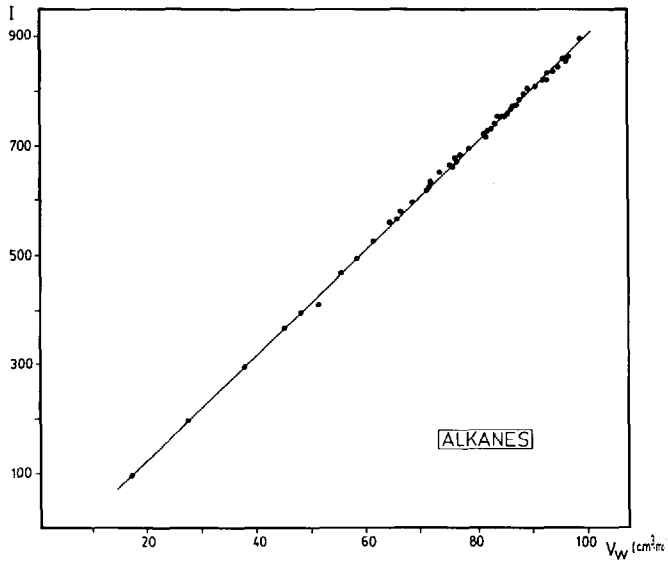


Fig. 4

alkanes. It also indicates the accuracy of the proposed method for the calculation of V_w.

The best equation for I vs. V_w should be obtained by linear regression resulting in:

$$I = -55.707 + 9.571\ V_w$$

$$N = 58 \quad R = 0.9992 \quad s = 7.04 \quad F = 33442.58$$

Conclusions

V_w and χ are linearly related which indicates that the two parameters are equivalent.

A general equation, $I = a\ V_w + b$, is applicable to all alkanes on squalane with a better correlation coefficient and statistics than the equivalent, $I = a'\chi + b'$.

A method for ready calculation of V_w of alkanes from group contributions is proposed. This method is capable of differentiating between isomeric alkanes.

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