Correlations Between Van der Waals' Volume and Retention Index General Equation Applicable to Different Homologous Series

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Key Words

Capillary gas chromatography
Retention index
Van der Waals' volume

Summary

Correlations between retention index (R_I) and Van der Waals' volume (V_w) in homologous series of n-alcohols, n-aldehydes and esters are studied on the stationary phases Carbowax 1540 and squalane. Influence of functional groups is quantified and a method for obtaining one general equation, valid for an indeterminate number of homologous series, is proposed.

Introduction

James and Martin [1] first observed that the logarithms of the specific retention volumes of homologous fatty acids gave a straight line when plotted against the number of carbon atoms (n) in the solute molecules. Since then, the same type of correlations have been applied to different homologous series in the study of equations concerning retention parameters and structural properties [2–4].

In a previous paper [5] we studied correlations between structure and retention index for esters, suggesting that steric and inductive effects have an influence on this chromatographic parameter. In the present paper correlations between Van der Waals' volume and retention index are studied for homologous series of n-alcohols, n-aldehydes and esters. A method to obtain a general equation capable of representing simultaneously different homologous series with a stationary phase is also proposed.

Experimental

Determination of retention index were carried out on two capillary columns of Carbowax 1540 and squalane. Standards, apparatus, experimental conditions, methods and data are described in earlier publications [5–7].

Calculations of Van der Waals' volumes were performed following the method proposed by Bondi [8] as a sum of the fragmentary values of the groups.

Values used were:

$$-H = 3.45,\quad -CH_3 = 13.67,\quad -CH_2- = 10.23,$$
$$>CH- = 6.78\ \mathrm{cm^3\,mol^{-1}}$$

Results and Discussion

James and Martin type equations ($R_I = an + b$) do not indicate the electric or steric nature of n. In order to evaluate these effects, plots of R_I against a steric parameter – Van der Waals' volume – were drawn. In all cases straight lines were obtained with excellent correlation coefficients, equal to or greater than those corresponding to R_I vs n. Some of these straight lines are plotted in Figs. 1 and 2 and equations for all of them are included in Table I.

From this table it can be deduced that:

1) in every homologous series the Van der Waals' volume is the principal parameter that has an influence on R_I, omitting the first members of each series. The influence of polar effects are not appreciable.

2) The slopes for all homologous compounds studied are between 9 and 10 in both stationary phases. Origin ordinate values show important variations (between 500–1100).

Deviations of the First Members of the Homologous Series

As can be observed in Table II deviations in the first plots for the equations R_I vs V_w have similar values depending only on the functional group.

The small size of the first members indicates that the +I inductive effect has a greater influence than the steric effect. This influence decreases with the length of the carbon chain until it becomes negligible, according to what is generally known about the propagation of electronic effects along carbon chains. This could be the cause of the deviations of the first terminus in our equations, R_I vs. V_w, and the James and Martin type equations.

Moreover, when the polarity of the functional group in a homologous series is smaller, the influence of the +I effect will be greater (Table II). Thus:

polar influence for n-alcohols < n-aldehydes < esters.

Variation of Slopes and Origin Ordinate for Equations R_I vs V_w

Similar values (9 to 10) of the slopes of the equations studied show that the influence of the Van der Waals' volume is of the same order regardless of the homologous series.

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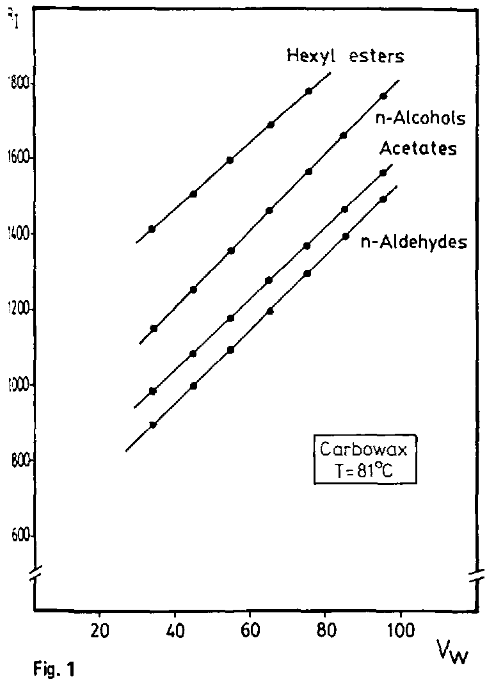

Fig. 1

Retention index (R_I) vs Van der Waals' volume (V_W). Carbowax1540 (Temp 81 °C)

Table I. Retention index (R_I) vs Van der Waals' volume (V_w) for homologous series (Temp 81 °C)

Homologous series	Carbowax	squalane
$-CH_2OH$	R_I = 800.99 + 10.23 V_w	R_I = 268.83 + 10.13 V_w
$-CHO$	R_I = 552.23 + 9.96 V_w	R_I = 196.73 + 10.00 V_w
HCOO–	R_I = 601.28 + 9.65 V_w	R_I = 219.47 + 10.03 V_w
MeCOO–	R_I = 655.31 + 9.58 V_w	R_I = 312.60 + 9.87 V_w
EtCOO–	R_I = 724.28 + 9.51 V_w	R_I = 414.17 + 9.73 V_w
nPrCOO–	R_I = 812.86 + 9.27 V_w	R_I = 509.21 + 9.62 V_w
nBuCOO–	R_I = 910.46 + 9.26 V_w	R_I = 612.88 + 9.50 V_w
nAmCOO–	R_I = 1008.03 + 9.12 V_w	–
nHexCOO–	R_I = 1130.20 + 8.55 V_w	–
–COOMe	R_I = 665.00 + 9.65 V_w	R_I = 328.96 + 9.79 V_w
–COOEt	R_I = 717.81 + 9.53 V_w	R_I = 409.29 + 9.69 V_w
–COOnPr	R_I = 808.16 + 9.42 V_w	R_I = 518.48 + 9.39 V_w
–COOnBu	R_I = 903.87 + 9.35 V_w	–
–COOnAm	R_I = 1008.83 + 9.13 V_w	–
–COOnHex	R_I = 1106.25 + 9.07 V_w	–
–COOiPr	R_I = 719.47 + 9.50 V_w	R_I = 451.38 + 9.62 V_w
–COOiBu	R_I = 846.15 + 9.33 V_w	R_I = 674.50 + 9.39 V_w
–COOiAm	R_I = 997.87 + 8.02 V_w	–

Correlation coefficients are greater than 0.9999 in all cases

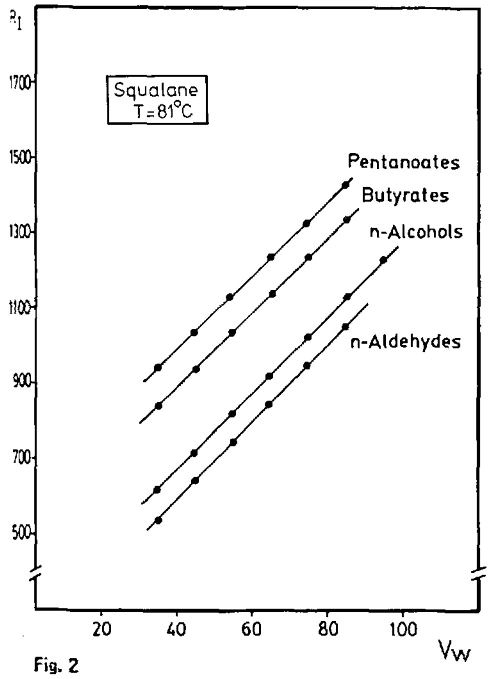

Fig. 2

Retention index (R_I) vs Van der Waals' volume (V_W). Squalane (Temp 81 °C)

Table II. Deviations in first plots for equations R_I vs. V_w. Carbowax 1540 (Temp 81 °C)

Homologous series	R	R_I (exp)	R_I (calc)	ΔR_I *
$R-CH_2OH$	H	914.4	836.3	+ 78.1
R–CHO	CH_3	632.1	688.4	– 56.3
	C_2H_5	806.8	790.3	+ 16.6
R–COOMe	H	767.0	698.3	+ 68.7
R–COOEt	H	831.4	750.7	+ 80.7
R–COOnPr	H	931.3	840.7	+ 90.6
R–COOnBu	H	1028.5	936.1	+ 92.4
R–COOnAm	H	1128.2	1040.3	+ 87.9
R–COOnHex	H	1227.2	1137.5	+ 89.7
			ΔR_I° =	+ 90.2
R–COOMe	CH_3	837.9	796.7	+ 41.0
R–COOEt	CH_3	895.8	848.1	+ 47.7
R–COOnPr	CH_3	982.2	936.9	+ 45.3
R–COOnBu	CH_3	1080.3	1031.7	+ 48.6
R–COOnAm	CH_3	1179.7	1133.6	+ 46.1
R–COOnHex	CH_3	1275.9	1230.2	+ 45.7
			ΔR_I** =	+ 46.7
R–COOMe	C_2H_5	912.6	895.6	+ 17.0
R–COOEt	C_2H_5	963.1	945.6	+ 17.5
R–COOnPr	C_2H_5	1050.6	1033.3	+ 17.3
R–COOnBu	C_2H_5	1146.1	1127.3	+ 18.8
R–COOnAm	C_2H_5	1243.4	1227.0	+ 16.4
R–COOnHex	C_2H_5	1340.6	1323.0	+ 17.6
			ΔR_I =	+ 17.4

(*) $\Delta R_I = R_I$ (exp) – R_I (calc) where R_I (exp) = experimental values of retention index and R_I (calc) = calculated value of retention index from eqs. R_I vs V_W

(°) Methyl formate and acetate have not been considered

(**) Methyl formate has not been considered

The origin ordinate represents the values of R_I when $V_w = 0$, that is, the contribution of the functional group (see Table I) to the R_I value. These values are very different (500–1100) depending on which homologous compounds is being considered.

Using the parameter P_I = origin ordinate/552.23, it is possible to assign a scale of influence on R_I of different groups relative to the –CHO group, where this parameter is 1. The values of P_I are shown in Table III.

The P_I values of the first plots are calculated by

$$P_{I\,(total)} = P_{I\,(funct.\,group)} + \Delta R_I/552.23$$

P_I values are shown in Table III and ΔR_I values in Table II. For example: $CH_3-COOEt$ (in Carbowax 1540)

$$P_I = P_{I\,(-COOEt)} + \Delta R_{I\,(-CH_3)}/552.23 = \\ = 1.30 + 47.7/552.23$$

$$P_I = 1.38$$

For the n-alcohols, the theoretical value would be 1.45 (Carbowax 1540), but it has been shown that the actual values are 10 % higher because the –OH groups are able to form hydrogen bonds. This increase corresponds to the difference between the conventional σ bond and hydrogen bond [9].

Table III. Relative influences of functional groups on R_I value

Functional Group	P_I (Carbowax)	P_I (squalane)
–CHO	1.00	1.00
$-CH_2OH$	1.60	1.50
–COOMe	1.21	1.67
–COOEt	1.30	2.08
–COOnPr	1.46	2.64
–COOnBu	1.64	–
–COOnAm	1.83	–
–COOnHex	2.00	–
–COOiPr	1.30	2.29
–COOiBu	1.53	3.43
–COOiAm	1.81	–
HCOO–	1.09	1.12
MeCOO–	1.19	1.59
EtCOO–	1.31	2.11
nPrCOO–	1.47	2.59
nBuCOO–	1.65	3.12
nAmCOO–	1.83	–
nHexCOO–	2.05	–

The P_I of the first plots are calculated from:

$$P_{I\,(total)} = P_{I\,(Funct.\,group)} + \Delta P_I \text{ (Table II)}$$

Eg. Ethyl acetate: (Carbowax 1540)

$$P_I = P_{I\,(-COOEt)} + \Delta P_{I\,(CH_3)} = 1.30 + 0.08 = 1.38$$

Branching chains always produce a reduction in P_I compared to linear chains with an equal number of carbon atoms. This influence is smaller the greater the branching of the functional group. Thus:

isopropyl < n-propyl $R_I = 0.16$
isobutyl < n-butyl $R_I = 0.11$
isopentyl < n-pentyl $R_I = 0.02$

Conclusions and General Equation

It can be concluded that:

a) V_w is the parameter that has the greatest influence on R_I values.

b) The relative influence of the functional group can be quantified by P_I, deduced by means of term b of the equations $R_I = aV_w + b$.

It is possible to combine both values (V_w and P_I) in order to obtain a general equation simultaneously applicable to all homologous series studied. Thus, in our case, the equations obtained are:

Squalane

$$R_I = 25.763 + 9.770\,V_w + 182.580\,P_I$$

$$N = 58 \quad R = 0.999 \quad s = 6.27 \quad F = 33674.78$$

Carbowax 1540

$$R_I = 86.024 + 9.507\,V_w + 486.736\,P_I$$

$$N = 95 \quad R = 0.998 \quad s = 14.62 \quad F = 10537.55$$

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

This method can be proposed for obtaining one valied equation in each stationary phase for an indeterminate number of homologous series simultaneously. These equations could be used to study the chromatographic behaviour of any organic compound.

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Received: May 29, 1981
Accepted: June 26, 1981
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