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Note

Relationship between gas chromatographic retention indices of homologous compounds and the number of carbon atoms and temperature

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The relationship between chromatographic retention parameters and column temperature has been studied with different homologous series of compounds on several stationary phases. Mitra and Saha[1] have summarized a number of early reports[2–4] and other papers have subsequently been published[5,6].

On the other hand, since the work of James and Martin[7], many studies of the correlation of retention data with the number of carbon atoms of homologous compounds and other structural parameters, at constant temperature, have been published. In a previous paper[8] we reported a study of the correlations between structure and retention indices of esters.

Generally, previous papers have related retention indices with temperature or structural parameters separately. Recently, Nóvak *et al.*[6] have proposed the possibility of correlating the logarithms of specific retention volumes of homologous compounds simultaneously with both the number of methylene groups and temperature.

The purpose of this work was to obtain equations that accurately correlate Kováts retention indices with both the number of carbon atoms and column temperature for homologous series of *n*-alkanols, *n*-alkanals and esters.

EXPERIMENTAL

Retention indices were determined with a Perkin-Elmer Model 900 chromatograph equipped with an SIP-1 digital integrator, a Model 56 counter and a flame-ionization detector. One stainless-steel capillary column (150 ft. × 0.01 in. I.D.) coated with Carbowax 1540–potassium hydroxide (99:1) was used.

The determinations were carried out at 70, 81, 90 and 126°C. Other experimental conditions were inlet pressure 930.9 torr, outlet pressure 760.0 torr, detector temperature 200°C, injector temperature 200°C, carrier gas nitrogen and sample size 0.04 μl.

The dead volume was determined by the Peterson and Hirsch method[9]. Retention indices were calculated by the statistical method proposed by Grobler and Bálizs[10]. For all determinations, a homologous series of *n*-alkanes (C_9–C_{14}) was used.

The retention indices were determined many times over a period of 3 years, and the values showed an average standard deviation of 0.02%. The graphs of retention index *versus* number of carbon atoms were straight lines (correlation coefficient = 0.9999).

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Most of the *n*-alkanols, *n*-alkanals and esters used were obtained from Merck (Darmstadt, G.F.R.), Fluka (Buchs, Switzerland) and Schuchard (Munich, G.F.R.). In some instances it was necessary to synthesize and purify them by normal laboratory methods.

RESULTS AND DISCUSSION

Fig. 1 shows the linear relationship between retention index and temperature for *n*-alkanols, *n*-alkanals and several homologous series of esters on Carbowax 1540.

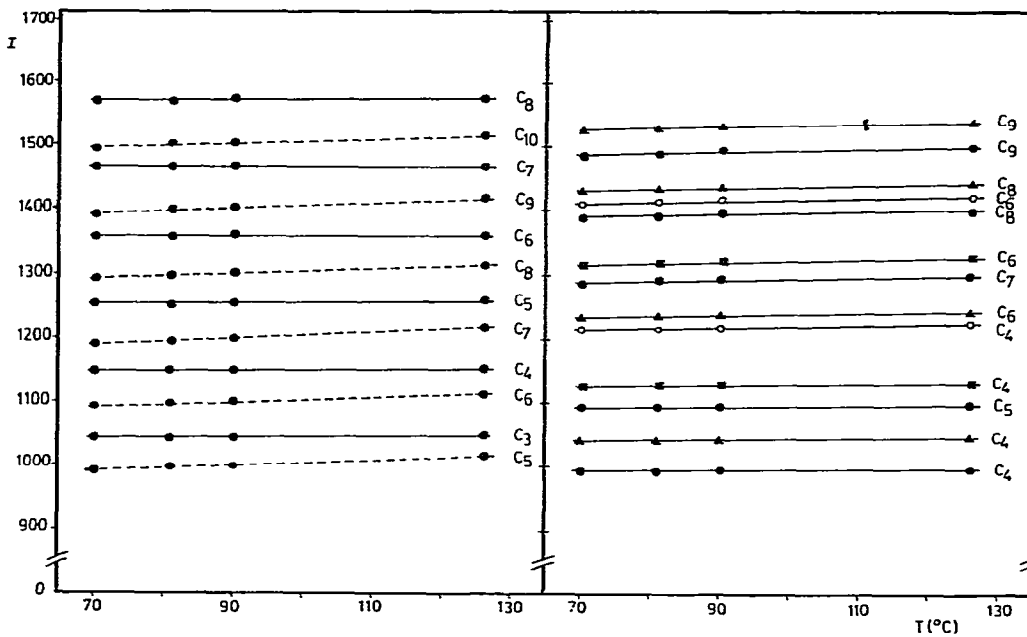

Fig. 1. Relationship between retention index (I) and temperature for *n*-alkanols (———) and *n*-alkanals (– – –) (left) and methyl (●), ethyl (▲), *n*-propyl (■) and *n*-butyl esters (○) (right). C_n = Total number of carbon atoms.

Table I presents the $\Delta I/10°C$ values corresponding to different substances in these series.

The *n*-alkanals show the greatest $\Delta I/10°C$ values and the *n*-alkanols the lowest, the esters having intermediate values.

With *n*-alkanols and *n*-alkanals the length of the carbon chain seems to have little influence on the $\Delta I/10°C$ value. With esters, however, an increase in chain length produces an increase in $\Delta I/10°C$.

Equations for I *versus* the number of carbon atoms at several temperatures are shown in Table II. There are no significant variations in the slope values at the different temperatures.

TABLE I

$\Delta I/10°C$ VALUES OF *n*-ALKANOLS, *n*-ALKANALS AND ESTERS ON CARBOWAX 1540

Temperature range: 70–126°C.

Homologous series	*Compound*	$\Delta I/10°C$	*Homologous series*	*Compound*	$\Delta I/10°C$
n-Alkanals	Butanal	4.9	Esters	Butyl hexanoate	2.7
	Pentanal	4.4		Butyl heptanoate	3.3
	Hexanal	3.6		Pentyl butyrate	2.4
	Heptanal	4.9		Pentyl pentanoate	2.8
	Octanal	4.2		Pentyl hexanoate	2.9
	Nonanal	4.2		Heptyl butyrate	3.1
	Decanal	4.1		Heptyl pentanoate	3.2
				Heptyl hexanoate	3.1
n-Alkanols	Propanol	0.8		Ethyl butyrate	1.3
	Butanol	0.9		Ethyl pentanoate	1.3
	Pentanol	1.0		Ethyl hexanoate	1.8
	Hexanol	0.6		Ethyl heptanoate	2.2
	Heptanol	0.7		Ethyl octanoate	2.4
	Octanol	0.6		Ethyl nonanoate	2.9
	Nonanol	0.5		Propyl butyrate	1.8
	Decanol	0.5		Propyl pentanoate	2.0
				Propyl hexanoate	2.5
Esters	Methyl butyrate	0.9		Propyl heptanoate	2.6
	Methyl pentanoate	1.3		Propyl octanoate	2.8
	Methyl hexanoate	2.7		Propyl nonanoate	3.3
	Methyl heptanoate	2.6		Hexyl butyrate	2.7
	Methyl octanoate	2.7		Hexyl pentanoate	2.7
	Methyl nonanoate	3.6		Octyl butyrate	3.4
	Methyl decanoate	3.6		Hexyl hexanoate	2.9
	Butyl butyrate	2.0		Octyl pentanoate	3.4
	Butyl pentanoate	2.6		Octyl hexanoate	3.3

TABLE II

EQUATIONS RETENTION INDEX (*I*) *VERSUS* NUMBER OF CARBON ATOMS (*n*) FOR HOMOLOGOUS SERIES

Correlation coefficient = 0.9999 in all instances.

Homologous series	*Equation*			
	70°C	*81°C*	*90°C*	*126°C*
n-Alkanols	$104.35\,n + 732.97$	$104.69\,n + 731.55$	$106.78\,n + 723.06$	$104.40\,n + 739.00$
n-Alkanals	$100.10\,n + 491.23$	$101.90\,n + 485.06$	$101.13\,n + 494.86$	$99.85\,n + 517.50$
Methyl esters	$97.68\,n + 506.60$	$98.72\,n + 501.69$	$100.27\,n + 495.18$	$100.40\,n + 498.23$
Ethyl esters	$96.38\,n + 464.30$	$97.49\,n + 458.10$	$98.87\,n + 450.72$	$98.20\,n + 459.91$
Propyl esters	$95.07\,n + 462.10$	$96.49\,n + 454.39$	$97.94\,n + 445.68$	$96.54\,n + 462.02$
Butyl esters	$93.99\,n + 467.98$	$95.65\,n + 457.75$	$96.96\,n + 449.73$	$96.20\,n + 462.10$

Equations for I versus number of carbon atoms and temperature

It is possible to study the influence of both temperature and the number of carbon atoms on the retention index together using equations of the form

$$I = an + bt + c$$

where I is the retention index, n is the number of carbon atoms, t (°C) is the column temperature and a, b and c are constants. The application of these equations to the homologous series studied led to the following expressions:

n-alkanols:

$I = 105.175n + 0.0705t + 723.456$

$N = 32$; $r = 0.9999$; $s = 3.686$; $F = 68371.88$

n-alkanals:

$I = 100.071n + 0.42181t + 458.575$

$N = 28$; $r = 0.9999$; $s = 2.525$; $F = 89225.79$

methyl esters:

$I = 99.067n_{ac} + 0.2378t + 579.204$

$N = 28$; $r = 0.9999$; $s = 3.070$; $F = 58364.88$

ethyl esters:

$I = 97.729n_{ac} + 0.2009t + 635.468$

$N = 28$; $r = 0.9999$; $s = 2.962$; $F = 61010.07$

n-propyl esters:

$I = 96.463n_{ac} + 0.2350t + 724.223$

$N = 28$; $r = 0.9998$; $s = 3.780$; $F = 36502.78$

n-butyl esters:

$I = 95.669n_{ac} + 0.2923t + 815.630$

$N = 28$; $r = 0.9998$; $s = 4.237$; $F = 28583.14$

where n_{ac} = total number of acid carbon atoms, N = number of compounds employed, r = correlation coefficient, s = standard deviation and F = experimental value from the Snedecor test.

From these equations it can be deduced that temperature has little influence on I compared with the number of carbon atoms present. The reliability of the equations is shown in Table III, which indicates that the maximal relative error between the theoretical and experimental values of the Kováts retention indices is 0.2%, which makes them very useful for the prediction or theoretical calculation of retention indices.

Finally, a general equation applicable to all esters was formulated:

$$I = 88.003n_{ac} + 88.260n_{al} + 0.1575t + 541.978$$

$N = 227$; $r = 0.9930$; $s = 27.45$; $F = 5275.42$

where n_{ac} is the number of acid carbon atoms and n_{al} is the number of alcohol carbon atoms. This equation, describing the general behaviour of esters, gave an average relative error of 1.6%. This higher error is a result of including short-chain esters, for which the deviations are similar to those which occur with the James and Martin type of equations.

TABLE III

COMPARISON BETWEEN *I* VALUES CALCULATED BY PROPOSED EQUATIONS AND EXPERIMENTAL DATA FOR *n*-ALKANOLS, ALKANALS AND ESTERS

E = relative error (%); *I* (exp) = experimental value of the retention indices; *I* (calc) = value calculated from equations proposed.

Compound	*70°C*			*81°C*			*90°C*			*126°C*		
	I (exp)	*I (calc)*	*E (%)*	*I (exp)*	*I (calc)*	*E (%)*	*I (exp)*	*I (calc)*	*E (%)*	*I (exp)*	*I (calc)*	*E (%)*
Propanol	1044.9	1043.9	−0.09	1039.5	1044.7	+0.50	1039.3	1045.3	+0.58	1049.4	1047.9	−0.15
Butanol	1151.3	1149.1	−0.19	1149.7	1149.9	+0.02	1149.6	1150.5	+0.08	1156.2	1153.1	−0.27
Pentanol	1256.3	1254.3	−0.16	1256.2	1255.0	−0.09	1258.1	1255.7	−0.19	1261.8	1258.2	−0.28
Hexanol	1357.7	1359.4	+0.13	1359.1	1360.2	+0.08	1363.1	1360.9	−0.16	1360.9	1363.4	+0.18
Heptanol	1463.4	1464.6	+0.08	1464.4	1465.4	+0.07	1470.4	1466.0	−0.30	1467.1	1468.6	+0.10
Octanol	1567.7	1569.8	+0.13	1569.1	1570.6	+0.09	1577.2	1571.2	−0.38	1571.6	1573.8	+0.14
Nonanol	1672.1	1675.0	+0.17	1673.8	1675.7	+0.12	1684.1	1676.4	−0.46	1675.1	1678.9	+0.23
Decanol	1776.4	1780.1	+0.21	1778.5	1780.9	+0.14	1790.8	1781.6	−0.52	1779.2	1784.1	+0.27
Butanal	890.6	890.9	+0.03	889.0	895.5	+0.73	900.0	899.3	−0.07	917.9	914.5	−0.37
Pentanal	992.7	991.6	−0.11	998.1	996.2	−0.19	1000.1	1000.0	0.00	1017.3	1015.2	−0.20
Hexanal	1092.4	1092.3	−0.01	1097.4	1097.0	−0.04	1101.5	1100.7	−0.07	1112.5	1115.9	+0.30
Heptanal	1191.7	1193.0	+0.11	1195.8	1197.7	+0.15	1202.1	1201.4	−0.05	1219.0	1216.6	−0.19
Octanal	1292.6	1293.7	+0.09	1300.3	1298.4	−0.15	1303.7	1302.1	−0.12	1315.8	1317.3	+0.12
Nonanal	1391.9	1394.4	+0.18	1400.6	1399.1	−0.11	1405.5	1402.9	−0.19	1415.3	1418.0	+0.19
Decanal	1492.2	1495.1	+0.19	1504.1	1499.8	−0.29	1505.9	1503.6	−0.16	1515.2	1518.7	+0.23

Methyl butyrate	994.0	992.1	−0.19	994.5	994.7	+0.02	996.9	996.9	0.00	999.1	1005.4	+0.63
Methyl pentanoate	1094.0	1091.2	−0.26	1094.9	1093.8	−0.10	1096.2	1095.9	−0.02	1101.4	1104.5	+0.28
Methyl hexanoate	1190.6	1190.3	−0.03	1192.5	1192.9	+0.03	1197.2	1195.0	−0.18	1205.9	1203.6	−0.19
Methyl heptanoate	1287.8	1289.3	+0.12	1292.6	1291.9	−0.05	1297.4	1294.1	−0.26	1302.4	1302.6	+0.02
Methyl octanoate	1385.5	1388.4	+0.21	1389.2	1391.0	+0.13	1397.5	1393.1	−0.31	1402.0	1400.8	−0.08
Methyl nonanoate	1482.7	1487.5	+0.32	1489.0	1490.1	+0.07	1497.6	1492.2	−0.36	1502.0	1500.8	−0.08
Methyl decanoate	1580.0	1586.5	+0.41	1587.5	1589.1	+0.10	1596.4	1591.3	−0.32	1600.4	1599.8	−0.04
Ethyl butyrate	1042.4	1040.4	−0.19	1043.1	1042.7	−0.04	1044.3	1044.5	+0.02	1049.4	1051.7	+0.22
Ethyl pentanoate	1140.2	1138.2	−0.18	1141.1	1140.4	−0.06	1142.9	1142.2	−0.06	1147.3	1149.4	+0.19
Ethyl hexanoate	1235.2	1235.9	+0.06	1263.3	1238.1	+0.15	1240.6	1239.9	−0.05	1245.3	1247.2	+0.15
Ethyl heptanoate	1331.8	1333.6	+0.13	1337.2	1335.8	−0.10	1341.2	1337.7	−0.27	1344.1	1344.9	+0.06
Ethyl octanoate	1428.5	1431.4	+0.20	1432.5	1433.6	+0.07	1440.8	1435.4	−0.38	1442.1	1442.6	+0.04
Ethyl nonanoate	1524.3	1529.1	+0.31	1530.4	1531.3	+0.06	1539.3	1533.1	−0.40	1540.4	1540.3	0.00
Ethyl decanoate	1620.4	1626.8	+0.39	1628.0	1629.0	+0.06	1637.1	1630.8	−0.38	1638.1	1638.1	0.00
n-Propyl butyrate	1127.9	1126.5	−0.12	1129.8	1129.1	−0.06	1131.6	1131.2	−0.03	1137.9	1139.7	+0.16
n-Propyl pentanoate	1223.0	1223.0	0.00	1227.8	1225.6	−0.18	1229.5	1227.7	−0.15	1234.3	1236.2	+0.15
n-Propyl hexanoate	1316.7	1319.5	+0.21	1320.0	1322.0	+0.15	1325.7	1324.2	−0.12	1330.9	1332.6	+0.13
n-Propyl heptanoate	1412.9	1415.9	+0.21	1420.7	1418.5	−0.15	1425.3	1420.6	−0.33	1427.5	1429.1	+0.11
n-Propyl octanoate	1508.3	1512.4	+0.27	1513.4	1515.0	+0.10	1523.4	1517.1	−0.42	1524.0	1525.5	+0.10
n-Propyl nonanoate	1602.2	1608.8	+0.41	1612.3	1611.4	−0.05	1620.9	1613.5	−0.46	1620.6	1622.0	+0.09
n-Propyl decanoate	1698.0	1705.3	+0.43	1708.7	1707.9	−0.05	1718.9	1710.0	−0.52	1716.7	1718.5	+0.10
n-Butyl butyrate	1220.2	1218.8	−0.12	1223.4	1222.0	−0.12	1227.1	1224.6	−0.20	1231.3	1235.1	+0.31
n-Butyl pentanoate	1314.2	1314.4	+0.02	1319.3	1317.7	−0.13	1323.4	1320.3	−0.24	1328.8	1330.8	+0.15
n-Butyl hexanoate	1407.1	1410.1	+0.21	1411.5	1413.3	+0.13	1419.5	1416.0	−0.25	1422.4	1426.5	+0.29
n-Butyl heptanoate	1501.6	1505.8	+0.28	1511.5	1509.0	−0.17	1513.3	1511.6	−0.11	1520.2	1522.1	+0.13
n-Butyl octanoate	1596.4	1601.4	+0.31	1605.5	1604.7	−0.05	1615.3	1607.3	−0.50	1616.7	1617.8	+0.07
n-Butyl nonanoate	1689.8	1697.1	+0.43	1701.2	1700.3	−0.05	1710.2	1703.0	−0.43	1712.9	1713.5	+0.03
n-Butyl decanoate	1783.8	1792.8	+0.50	1796.8	1796.0	−0.04	1807.2	1798.6	−0.48	1809.1	1809.2	0.00

CONCLUSIONS

Retention indices for several series of homologous compounds on Carbowax 1540 can be expressed as a function of the number of carbon atoms and the column temperature. These relationships have the advantage of including in a single equation, without employing empirical parameters, the two principal factors that determine retention indices. Generally, these factors are studied separately. These equations may be used for the prediction or theoretical calculation of retention indices, as the relative errors are low.

REFERENCES

1 G. D. Mitra and N. C. Saha, *Chromatographia*, 6, No. 2 (1973) 93.
2 J. S. Ettre and K. Billeb, *J. Chromatogr.*, 30 (1967) 1, 12.
3 J. Takács, M. Rockenbauer and I. Olácsi, *J. Chromatogr.*, 42 (1969) 19.
4 N. C. Saha and G. D. Mitra, *J. Chromatogr. Sci.*, 8 (1970) 84.
5 G. Castello, M. Berg and M. Lunardelli, *J. Chromatogr.*, 79 (1973) 23.
6 J. Novák, J. Vejrosta, M. Roth and J. Janák, *J. Chromatogr.*, 199 (1980) 209.
7 A. T. James and A. J. P. Martin, *Biochem. J.*, 50 (1952) 679.
8 F. Saura Calixto and A. García Raso, *Chromatographia*, 14, No. 3 (1981) 143.
9 M. L. Peterson and J. Hirsch, *J. Lipid. Res.*, 1 (1959) 1932.
10 A. Grobler and G. Bálizs, *J. Chromatogr. Sci.*, 12 (1974) 57.