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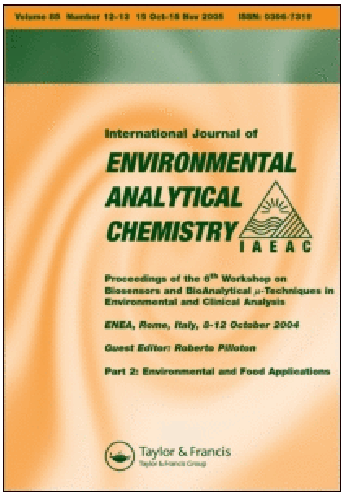

International Journal of Environmental Analytical Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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To cite this Article Bermejo, J. and Guillen, M. D.(1985) 'Biparameter Equations for Calculating Kovats Retention Indices of Hydrocarbons', International Journal of Environmental Analytical Chemistry, 23: 1, 77 — 86
To link to this Article: DOI: 10.1080/03067318508076436
URL: http://dx.doi.org/10.1080/03067318508076436

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Intern. J. Environ. Anal. Chem., 1985, Vol. 23, pp. 77–86
0306-7319/85/2302-0077 $18.50/0

Printed in Great Britain

Biparameter Equations for Calculating Kováts Retention Indices of Hydrocarbons[†]

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(*Received January 15, 1985; in final form May 25, 1985*)

Biparameter equations, in which one parameter is the boiling point of the solutes and the other is any of their physicochemical properties able to account for dispersive solute-stationary phase interactions, are obtained by regression analysis. These equations permit the calculation of Kováts retention index (I_R) for aliphatic and aromatic hydrocarbons in complex mixtures with standard deviations close to experimental error. The linear change of regression coefficients with the work temperature allow us to obtain equations suitable for calculating I_R at any temperature on a given stationary phase. Furthermore, accurate values for the magnitudes included in the equations can be obtained starting from I_R values.

When alkylbenzenes are separated on polar phases, such as Carbowax 20M, it is necessary to add a new parameter accounting for inductive interactions. Once again, regression coefficients, except that of the boiling point which remains constant, change linearly with the polarity of the phase (Tarjan's scale) enabling the obtaining of an equation for calculating I_R on any stationary phase at a given work temperature, although constant deviations between calculated and experimental I_R, on polymeric stationary phases, are found.

KEY WORDS: Hydrocarbons, structure-retention relationships, Kováts retention index, gas chromatography.

[†] Presented at the 2nd Workshop on Chemistry and Analysis of Hydrocarbons in the Environment, Barcelona, November 19–20, 1984.

INTRODUCTION

Chromatographic retention parameters give limited information on the nature of the solutes. Works carried out for establishing relationships between structural properties and gas-chromatographic parameters of solutes have led to some practical but limited applications.[1-6] Since chromatographic retention is a consequence of solute-stationary phase interactions, some physicochemical properties or structural parameters which might account for these interactions have been related to Kováts retention index (I_R), but, with the exception of compounds of homologous series, the results obtained have been unsatisfactory with regard to the prediction of I_R.[7-8]

The application to gas chromatography (GC) of the dielectric approach based on the theory of non-specific solvation[9] leads to Eq. (1) for I_R,

$$I_R = I_R^0 + pP + qQ + rR + \cdots \tag{1}$$

in which I_R^0 would be the retention index of the solutes in the absence of solute-stationary phase interactions; P, Q, R, . . . represent independent but complementary solute parameters which account for the different interaction mechanisms such as dispersion, induction, orientation, and other effects; and p, q, r, . . . are the regression coefficients which describe the sensitivity of the retention process to the different solute-phase interaction mechanisms.

Since I_R^0 is linearly related to the boiling point (T_b), Eq. (1) takes the general form of

$$I_R = m + nT_b + pP + qQ + rR + \cdots. \tag{2}$$

When the polarity of solutes is low as in the case of the hydrocarbons, and they are separated on non-polar or low-polar phases, mainly dispersive interactions must be expected. Therefore Eq. (2) can be reduced to Eq. (3) in which P represents any parameter or physicochemical property accounting for dispersive solute-phase interactions. This

$$I_R = m + nT_b + pP \tag{3}$$

kind of interaction is related to electronic polarisability of solutes and therefore to structural parameters or physicochemical properties such as their first-order molecular connectivity (χ), van der Waal's volume (V_W), molar volume (V_M), and molar refraction (R_M).[10-11] In this paper we report the equations obtained by regressing I_R, T_b and P of different families of hydrocarbons and their possible applications.

EXPERIMENTAL

Retention indices were taken from the literature.[12-14] Boiling points, refractive indices (n_D), and densities were taken also from the literature.[15] Molar refraction, van der Waal's volume, and molecular connectivity were calculated according to Lorentz–Lorentz, Bondi,[16] and Randic[17] expressions, respectively. The molar volume is the ratio between molecular weight and density at 20°C. Regression coefficients and statistics were calculated by a multiple regression linear program in a HP 1000 computer.

RESULTS

The attempts to establish relationships between I_R of aliphatic and aromatic hydrocarbons and their T_b and P were not successful. However, when data introduced in Eq. (3) belonged to compounds of a given family, the equations obtained exhibited standard deviations close to the experimental error. Thus, for a population of 7 linear alkanes from C_3 to C_9 carbon atoms; 33 methyl- and ethyl-branched alkanes, from C_5 to C_9, with one or more appendages; and 15 cyclic alkanes, which include *cis* and *trans* isomers, from cyclobutane to cyclooctane, some of them with methyl-, ethyl-, propyl-, or isopropyl- groups, and using I_R at 50°C on Squalane[14] the equations shown in Table I were obtained. Regression coefficients of the four equations change in parallel with the temperature and the polarity of the phase, from which it may be deduced that the parameters used have similar chromatographic meaning. Regression coefficients of equations $I_R = f(T_b, R_M)$ change linearly with the column temperature (Table II), therefore it is possible to establish an equation for calculating I_R of alkanes at any temperature within this

TABLE I

Equations $I_R = f(T_b, P)$, where $P = V_W$, V_M, χ, or R_M for 7 lineal (C_3–C_9), 15 cyclic (C_5–C_8), and 33 branched (C_5–C_9) alkanes

Equations	R	s	N
$I_R = 192.44 + 3.96T_b + 967.05(10/V_W)$	0.9989	5.5	55
$I_R = 244.53 + 3.65T_b + 1480.86(10/V_M)$	0.9972	8.8	55
$I_R = 122.81 + 4.33T_b + 52.14(10/\chi)$	0.9973	8.7	55
$I_R = 156.38 + 4.12T_b + 498.84(10/R_M)$	0.9995	3.7	55

R is the correlation coefficient, s standard deviation, and N number of experimental points.

TABLE II

Equations $I_R = f(T_b, R_M)$ for alkanes at several temperatures

t (°C)	Equations	R	s	N
27	$I_R = 181.63 + 3.98T_b + 446.40(10/R_M)$	0.9994	3.9	46
50	$I_R = 163.91 + 4.08T_b + 484.24(10/R_M)$	0.9995	3.7	47
67	$I_R = 161.42 + 4.09T_b + 492.36(10/R_M)$	0.9994	4.0	47
86	$I_R = 138.27 + 4.21T_b + 541.04(10/R_M)$	0.9991	5.1	47

All definitions are as in Table I.

range. For example, with data obtained from equations in Table II, Eq. (4) was obtained

$$I_R = 200.72 + 3.88T_b + 4042.56(1/R_M) + [0.0036T_b + 15.09(1/R_M) - 0.69]t. \quad (4)$$

This equation allows the prediction of the I_R values of alkanes on Squalane at any temperature with a standard deviation of 4.1 close to the common experimental error.

When the same approach was applied to a group of 40 alkenes and 10 alkynes satisfactory relations between I_R, T_b and P (P being also $= R_M$, V_W, V_M, or χ) were obtained. The family of alkenes consists of C_4 to C_8 carbon atoms alkenes, with only one double bond and methyl- and ethyl-appendages. *Cis*- and *trans*-isomers are also included. Alkynes have only one triple bond; they are linear alkynes between C_4 to C_7 except a methyl substituted hexyne. Table III shows the equations obtained from I_R on Squalane at 49°C.

These relationships permit the accurate calculation of magnitudes included in the equations. For example, retention indices of several alkenes and alkynes, not included in the regression analyses (from which the equations in Table II were obtained) were calculated from equations which contain V_W, an easily calculable structural parameter. The calculated indices are very close to the experimental ones (see Table IV). Accurate values of R_M can also be obtained from I_R and T_b. They are also shown in Table IV together with those calculated by the additive method of Vogel.[18]

TABLE III

Equations $I_R=f(T_b,P)$, where $P=R_M$, V_M, V_W, or χ for C_4–C_8 alkenes, and C_4–C_7 alkynes

Familie	Equations	R	s	N
Alkenes	$I_R=247.65+3.67T_b+312.19(10/R_M)$	0.9990	3.4	40
	$I_R=272.29+3.49T_b+1155.93(10/V_M)$	0.9986	3.9	40
	$I_R=249.22+3.67T_b+675.71(10/V_W)$	0.9989	3.6	40
	$I_R=256.30+3.73T_b+223.12(1/\chi)$	0.9985	4.1	40
Alkynes	$I_R=120.48+4.42T_b+420.38(10/R_M)$	0.9994	3.1	10
	$I_R=156.31+4.18T_b+1525.59(10/V_M)$	0.9994	3.1	10
	$I_R=123.93+4.38T_b+965.79(10/V_W)$	0.9994	3.2	10
	$I_R=233.55+4.06T_b+153.63(1/\chi)$	0.9986	4.7	10

All definitions are as in Table I.

TABLE IV

I_R and R_M values calculated from equations in Table III for alkenes and alkynes

Compound	T_b (°C)	V_W (ml/mol)	I_{R_c}	$I_{R_c}^{12}$	R_M (ml/mol)	R_M^{18} (ml/mol)
cis-2-butene	3.70	44.28	415.4	417.0	20.04	20.16
trans-2-butene	0.88	44.28	405.0	405.0	20.26	20.16
2-methyl-1-propene	−6.90	44.29	376.5	383.0	19.43	20.16
trans-2-hexene	67.87	64.74	602.7	597.0	31.13	29.46
Acetylene	−84.00	23.10	174.1	156.8	10.31	9.22
1-butyne	8.10	43.50	381.4	385.3	18.36	18.51
4-methyl-1-pentyne	61.70	63.95	550.7	552.0	26.47	27.80

The group of 34 alkylbenzenes, listed in Table VII, gives the equations shown in Table V, from I_R on Squalane or Ucon LB 550X, at 100°C. The standard deviation is also close to the experimental error.

When more polar phases are used, such as Carbowax 20M, inductive interactions between the stationary phases and alkylbenzenes must be considered, and equations for I_R have to include a new parameter which accounts for this kind of interaction. Inductive interactions have been related to the ratio between R_M and the molar volume at boiling point.[19] Furthermore, the introduction of functions of the refractive index n_D in the regression analysis causes decreasing of standard deviations of I_R of alkylbenzenes on polar stationary phases.[10] Therefore the parameter $(n_D^2-1)/(n_D^2+2)$ is utilized.

TABLE V

$I_R=f(T_b, P)$, where $P=R_M$, χ, V_M, or V_W for alkylbenzenes

Phase	Equations	R	s	N
Squalane	$I_R=61.79+4.68T_b+546.64(10/R_M)$	0.9995	3.9	34
	$I_R=120.11+4.57T_b+314.44(1/\chi)$	0.9995	3.6	34
	$I_R=113.50+4.54T_b+1482.65(10/V_M)$	0.9994	4.1	34
	$I_R=61.84+4.74T_b+1010.19(10/V_W)$	0.9995	3.7	34
Ucon LB 550X	$I_R=-62.71+5.29T_b+1047.72(10/R_M)$	0.9995	3.8	34
	$I_R=59.59+5.05T_b+584.95(1/\chi)$	0.9994	4.2	34
	$I_R=25.35+5.04T_b+2926.36(10/V_M)$	0.9996	3.5	34
	$I_R=-38.05+5.32T_b+1834.97(10/V_W)$	0.9991	5.2	34

All definitions are as in Table I.

TABLE VI

Equations $I_R=f(T_b, V_W, n_D)$ for alkylbenzenes on phases of different polarity

Phase	Equations	R	s	N
1	$I_R=40.61+4.69T_b+954.45(10/V_W)+120.55D$	0.9995	3.7	34
2	$I_R=-258.73+4.87T_b+1255.55(10/V_W)+1253.25D$	0.9996	3.3	34
3	$I_R=-478.21+4.92T_b+1366.61(10/V_W)+2120.27D$	0.9996	3.5	34
4	$I_R=-1015.82+4.83T_b+1456.17(10/V_W)+4359.85D$	0.9986	6.3	34

All definitions are as in Table I. Phase 1, Squalane; Phase 2, Ucon LB 550X; Phase 3, Ucon 50 HB 280X; and Phase 4, Carbowax 20M.

TABLE VII

Experimental and predicted by Eq. (5) I_R values for alkylbenzenes on several phases

Compound	Squalane			Ucon LB 550X			Ucon 50 HB 280X			Carbowax 20M		
	I_{R_e}	I_{R_c}	ΔI_R	I_{R_e}	I_{R_c}	ΔI_R	I_{R_e}	I_{R_c}	ΔI_R	I_{R_e}	I_{R_c}	ΔI_R
BZ	650.5	645.5	+5.0	759.2	776.0	−16.8	821.5	827.2	−5.7	947.2	941.7	+5.5
1MBZ	760.1	754.7	+5.4	862.1	871.9	−9.8	919.9	917.8	+2.1	1043.2	1020.6	+22.6
1EBZ	850.0	853.8	−3.8	950.3	965.3	−15.0	1007.2	1008.9	−1.7	1127.1	1106.7	+20.4
14MMBZ	864.6	862.1	+2.5	960.5	973.1	−12.6	1017.2	1016.5	+0.7	1134.8	1113.8	+21.0
13MMBZ	864.8	865.8	−1.0	963.9	978.1	−14.2	1021.7	1022.1	−0.4	1140.7	1120.5	+20.2
12MMBZ	886.0	890.6	−4.6	991.6	1010.5	−18.9	1053.4	1057.5	−4.1	1183.9	1162.7	+21.2
1I3BZ	908.4	914.3	−5.9	1004.4	1017.5	−13.1	1059.5	1058.0	+1.5	1169.8	1148.4	+21.4
13BZ	938.0	947.1	−9.1	1036.6	1050.8	−14.2	1092.4	1091.4	+1.0	1205.4	1182.3	+23.1
13EMBZ	949.7	955.3	−5.6	1047.5	1063.0	−15.5	1105.4	1105.1	+0.3	1219.1	1199.5	+19.6
14EMBZ	954.3	958.8	−4.5	1047.5	1065.8	−18.3	1105.4	1107.7	−2.3	1219.1	1201.5	+17.6
135MMMBZ	969.0	970.2	−1.2	1065.9	1080.1	−14.2	1122.8	1123.2	−0.4	1236.9	1219.6	+17.3
12EMBZ	966.0	973.3	−7.3	1069.0	1088.4	−19.4	1130.7	1133.5	−2.8	1254.4	1234.4	+20.0
1T4BZ	971.7	980.2	−8.5	1067.7	1081.4	−13.7	1123.1	1121.0	+2.1	1229.5	1209.7	+19.8
124MMMBZ	987.0	991.7	−4.7	1089.9	1106.7	−16.8	1149.8	1151.7	−1.9	1272.2	1252.5	+19.7
1I4BZ	991.3	999.2	−7.9	1083.8	1094.6	−10.8	1133.9	1132.0	+1.9	1235.9	1215.7	+20.2
1S4BZ	990.2	999.8	−9.6	1085.0	1098.6	−13.6	1138.1	1137.3	+0.8	1241.7	1223.9	+17.8
13MI3BZ	1009.9	1008.5	+1.4	1101.9	1109.7	−7.8	1155.6	1149.4	+6.2	1260.4	1238.0	+22.4
123MMMBZ	1012.9	1023.1	−10.2	1123.1	1146.5	−23.3	1188.6	1194.8	−6.2	1320.6	1302.9	+17.7
13EEBZ	1027.4	1036.8	−9.4	1125.5	1140.3	−14.8	1181.6	1180.8	+0.8	1289.4	1271.6	+17.8

TABLE VII (continued)

Compound	Squalane			Ucon LB 550X			Ucon 50 HB 280X			Carbowax 20M		
	I_{R_e}	I_{R_c}	ΔI_R	I_{R_e}	I_{R_c}	ΔI_R	I_{R_e}	I_{R_c}	ΔI_R	I_{R_e}	I_{R_c}	ΔI_R
14BZ	1036.8	1048.1	−11.3	1134.2	1146.5	−12.3	1191.8	1185.1	+6.7	1301.9	1271.4	+30.5
14M3BZ	1040.2	1046.8	−6.6	1134.6	1146.9	−11.9	1188.4	1186.2	+2.2	1296.0	1273.9	+22.1
14EEBZ	1040.5	1050.1	−9.6	1135.4	1154.8	−19.4	1190.1	1196.6	−6.5	1289.4	1287.5	+1.9
12M3BZ	1045.6	1055.6	−10.0	1146.5	1163.1	−16.6	1206.7	1205.3	+1.4	1321.5	1299.5	+22.0
124MEMBZ	1062.2	1063.2	−1.0	1162.6	1174.7	−12.1	1220.7	1218.3	+2.4	1335.0	1316.0	+19.0
124MMEBZ	1072.7	1076.9	−4.2	1173.6	1187.2	−13.6	1233.5	1230.4	+3.1	1350.5	1327.1	+22.9
1245MMMMBZ	1107.1	1109.2	−2.1	1214.2	1227.2	−13.0	1277.1	1273.4	+3.7	1401.3	1376.7	+24.6
1235MMMMBZ	1113.1	1114.9	−1.8	1221.0	1234.1	−13.1	1284.8	1280.8	+4.0	1410.5	1385.3	+25.2
13I3I3BZ	1120.5	1124.7	−4.2	1205.5	1216.9	−11.4	1254.1	1253.1	+1.0	1342.2	1334.0	+8.2
14E3BZ	1126.4	1141.9	−15.5	1218.5	1239.8	−21.3	1272.5	1278.2	−5.7	1374.1	1363.9	+10.2
1234MMMMBZ	1138.6	1147.9	−9.3	1251.9	1273.9	−22.0	1320.7	1323.2	−2.5	1456.0	1433.6	+22.4
15BZ	1133.0	1145.3	−12.3	1233.2	1239.3	−6.1	1289.0	1276.1	+12.9	1394.1	1358.6	+35.5
14M4BZ	1138.8	1151.7	−12.9	1233.6	1249.1	−15.5	1288.1	1287.2	+0.9	1391.6	1372.6	+19.0
14I3I3BZ	1154.1	1158.8	−4.7	1239.3	1252.5	−13.2	1288.9	1289.2	−0.3	1380.7	1371.3	+9.4
12345MMMMMBZ	1260.1	1266.2	−6.1	1381.7	1395.6	−13.9	1451.7	1446.3	+5.4	1591.6	1559.8	+31.8

Abbreviations: M = methyl; E = ethyl; 3 = *n*-propyl; I3 = isopropyl....

By regressing I_R, T_b, V_W, and $(n_D^2-1)/(n_D^2+2)$ of the aforementioned alkylbenzenes on phases of polarity between 0 and 70.75 in the Tarjan's scale,[20] the equations shown in Table VI are obtained. Regression coefficients of these equations change linearly with the polarity of the stationary phase, except the boiling temperature coefficient n, which remains constant, consequently Eq. (5), which includes the polarity of the stationary phase, can be obtained in which $D=(n_D^2-1)/(n_D^2+2)$, and P_T is the polarity of the stationary phase in the Tarjan's scale

$$I_R=113.73+4.83T_b+995.91(10/V_W)-207.31D$$
$$+[7.22(10/V_W)+59.74D-14.91]P_T. \qquad (5)$$

I_R values of alkylbenzenes obtained from Eq. (5) are close to the experimental values on Squalane and on Ucon 50HB 280X ($P_T=43.41$) (see Table VII), but they are about 14 units higher and 20 units lower than those on Ucon LB 550X and Carbowax 20M respectively. These results show again that polymeric stationary phases are difficult to characterize. These deviations reflect, probably, differences between the tabulated and real polarity of these stationary phases.

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