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Sensitivity of the methylbenzenes and chlorobenzenes retention index to column temperature, stationary phase polarity, and number and chemical nature of substituents

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Abstract

Retention indices of methylbenzenes and chlorobenzenes on two fused silica capillary columns, HP-5 (diphenylsiloxane 5% diphenyldimethylsiloxane) and ZB-WAX (polyethylene glycol), have been calculated at various isothermal temperatures and compared with literature data. The retention index temperature effect was studied for each solute, finding greater retention index the higher the column temperature. A comparison between the straight line fit and the fit to the recently proposed equation $I = A + B/T + C \ln T$ was carried out. The effect of the stationary phase polarity on the retention index was checked. In general, a greater retention index was found for the more polar stationary phase. The retention indices of the chlorobenzenes are greater than the retention indices of the methylbenzenes, irrespective of the stationary phase and the column temperature. In addition, the influence of the methyl/chlorine substitution on the benzene molecule was investigated at each temperature. The retention indices increased as the number of substituents (methyl/chlorine) increased. The retention index increments of methyl and chloro derivatives are also discussed, which permits to compare the effect of both, methyl or chlorine, chemical functions, for a fixed substituent number in the benzene molecule.

Keywords: Methylbenzenes; Chlorobenzenes; HP-5 and ZB-WAX; Retention index temperature effect; Stationary phase effect; Substituent effect; Retention index increments

1. Introduction

Methylbenzenes and chlorobenzenes are important compounds in chemical industry, as hazard compounds, fungicides, pollutants, etc.

Retention indices of chlorobenzenes were determined in 1983 by Haken et al. [1] at several temperatures on the unequally polar SE-30 and Carbowax 20M stationary phases. Taking monochlorobenzene as reference, the authors studied the influence of the chlorination extent on the retention index increments, i.e., the difference between the retention index (I) of the chlorobenzenes and of monochlorobenzene, of these solutes. Also, Castello et al. [2] determined retention factors of chlorobenzenes on several stationary phases of different polarity, as SPB-1 and Wax. In this work the retention indices of chlorobenzenes were determined at 120–180 °C on a fused silica capillary column coated with polyethylene glycol as stationary phase (ZB-WAX).

The retention indices of the twelve methylbenzenes were determined among a broad bunch of alkylbenzenes [3–14], very often at a single temperature, and in some cases on the zero polarity stationary phase squalane [3–8]. Determinations of benzene and toluene on DB-1, DB-5 and DB-WAX were recently reported [26–28].

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The aims of this work are the determination of the retention indices of benzene, the 12 methylbenzenes and the chlorobenzenes on the above stationary phases over a wide temperature range. Furthermore, the investigation of the temperature effect on the retention index, the effect of the polarity of the stationary phase on the retention index, and the influence of the number/chemical nature of substituents on the retention index were studied at each temperature.

At the same time, the dependence of the slope and intercept on the extent of methylation and chlorination of the two series of methylbenzenes and isomeric chlorobenzenes was checked.

Finally, these compounds on both stationary phases at different temperatures are discussed in terms of the comparison of the retention index increments propounded by Haken et al. [1] for chlorobenzenes and by Macák et al. [8] for methylbenzenes.

2. Experimental

The fused silica capillary columns used were: HP-5 (60 m × 0.25 mm i.d. × 0.25 μm) coated with cross-linked diphenylsiloxane (5%) diphenyldimethylsiloxane, and ZB-WAX (60 m × 0.25 mm i.d. × 0.25 μm) coated with cross-linked polyethylene glycol stationary phase, purchased from Zebron GLC columns from Phenomenex (USA).

Solutes, the standard *n*-alkanes; benzene; methylbenzenes and chlorobenzenes were obtained from different suppliers [Riedel-de Häen, Fluka, Aldrich, Sigma and Protocol Analytical (USA)]. A purity of 98–88% sufficed for chromatographic use.

Gas chromatograph was an HP 5890 equipped with a flame ionization detection (FID) system, the carrier gas flow-rate being 1 $cm^3\ min^{-1}$ of nitrogen.

The EXCEL utility was used for the calculations. Microcal Origin 6.0 was used for the linear regressions. Methane, the unretained substance for the hold-up time, and a homologous series of standard *n*-alkanes were used to obtain the retention indices. Retention factors were used as retention datum to calculate the retention index, according to Kováts equation [16]:

$$I(x) = 100\left[z + \frac{log(k_x/k_z)}{log(k_{z+1}/k_z)}\right] \quad (1)$$

where

$$k = \frac{t_R - t_M}{t_M} \quad (2)$$

t_R being the retention time measured from the chromatograms and t_M the hold up time, measured for methane in the same chromatogram.

k_x, k_z and k_{z+1} are the retention factors of the analyte, and of the *n*-alkanes eluting before and after the peak of solute *x*. Retention times were averaged for at least five injections for each compound.

3. Results and discussion

The retention indices of benzene and the methlbenzenes obtained in this work with Eq. (1) from the retention times measured in the chromatograms on HP-5 and ZB-WAX, at 100–160 °C, are given un Table 1, and the retention indices of the chlorobenzenes on ZB-WAX at 120–180 °C are summarized in Table 2, while retention indices and retention factors of the chlorobenzenes on HP-5 at the same temperature range were taken from refs. [17,18]. The retention index values are compared graphically with the Kováts indices reported from the literature [1,2,17].

Fig. 1 shows the plot of the retention indices, *I*, of the 12 chlorobenzenes recently reported [17], those obtained in this work at 140 °C, and those obtained by Haken et al. [1] in the last eighties, and those obtained by one of us [19]. The lower straight line shows a good agreement between the nonpolar stationary phases HP-5 [17] and SE-30 [1,19], the last two retention index values are closer because they are the same SE-30, since HP-5 is slightly more polar. The upper straight line shows greater differences, about 2-3%, between the retention indices obtained on ZB-WAX (this work) and those values taken from the literature [1].

Fig. 2 shows the retention indices of benzene and the methylbenzenes determined on nonpolar stationary phases and the *I* values determined on HP-5 (this work) at 100 °C [7,10–12,15,19].

Fig. 3 shows the similar plot for the retention indices of benzene and methylbenzenes on polyethylene glycols obtained on ZB-WAX (this work) and those reported in the literature [7,10,13,14,20].

If PEG 400 [20] is disregarded, the discrepancies are reasonable bearing in mind that the retention indices of these substances have been determined in different laboratories with different chromatographic columns and different gas

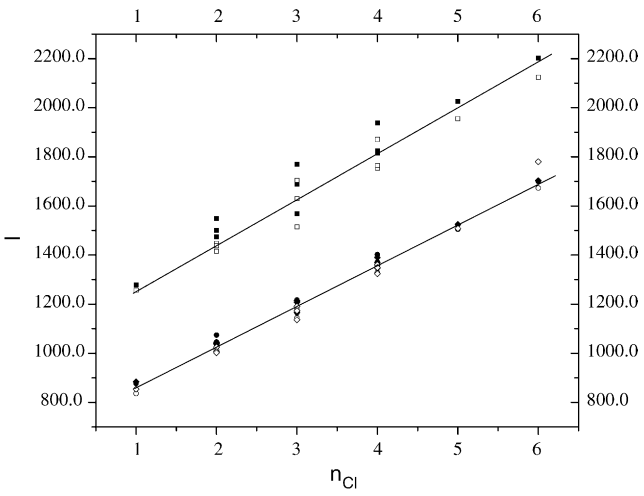

Fig. 1. Comparison of the retention indices of chlorobenzenes at 140 °C. Retention index source: (■), ZB-WAX (this work) (□), Carbowax 20M, ref. [1] (●), HP-5, ref. [17] (○), SE-30, ref. [1] (♦), HP-5, ref. [19] (◊), SE-30, ref. [19].

Table 1
Measured retention indices of benzene and the methylbenzenes on HP-5 and ZB-WAX at 100–160 °C

Solute	HP-5				ZB-WAX			
	100 °C	120 °C	140 °C	160 °C	100 °C	120 °C	140 °C	160 °
Benzene	678.8 ± 0.5	683.3 ± 1.0	687.4 ± 1.4	694.6 ± 3.0	979.4 ± 0.7	988.6 ± 0.9	999.5 ± 1.5	1010.4 ± 1.1
Methylbenzene	782.2 ± 0.5	787.7 ± 0.9	791.0 ± 1.1	798.9 ± 3.5	1077.5 ± 0.3	1088.3 ± 0.4	1099.4 ± 0.6	1112.0 ± 0.9
1,2-Dimethylbenzene	908.3 ± 0.3	915.1 ± 0.6	922.8 ± 1.6	929.2 ± 3.0	1221.0 ± 0.3	1234.3 ± 0.35	1248.5 ± 1.0	1262.1 ± 1.4
1,3-Dimethylbenzene	882.7 ± 0.4	888.1 ± 0.6	895.0 ± 1.6	899.8 ± 0.9	1176.5 ± 0.3	1188.1 ± 0.3	1200.4 ± 1.2	1212.8 ± 1.8
1,4-Dimethylbenzene	883.2 ± 0.4	888.1 ± 0.7	892.7 ± 0.4	900.8 ± 3.4	1169.5 ± 0.4	1180.4 ± 0.3	1193.3 ± 0.7	1205.0 ± 1.5
1,2,3-Trimethylbenzene	1035.4 ± 0.1	1043.5 ± 0.2	1053.3 ± 0.3	1061.0 ± 0.6	1366.3 ± 0.2	1382.9 ± 0.1	1400.2 ± 0.6	1417.0 ± 1.1
1,2,4-Trimethylbenzene	1005.5 ± 0.2	1012.3 ± 0.3	1019.4 ± 0.6	1026.8 ± 0.75	1312.4 ± 0.1	1326.7 ± 0.1	1341.5 ± 0.9	1355.5 ± 1.1
1,3,5-Trimethylbenzene	979.5 ± 0.1	984.8 ± 0.3	990.8 ± 1.0	996.4 ± 2.9	1275.1 ± 0.2	1287.3 ± 0.2	1300.7 ± 0.6	1312.9 ± 1.4
1,2,3,4-Tetramethylbenzene	1159.8 ± 0.2	1169.4 ± 0.15	1179.3 ± 0.3	1189.4 ± 0.3	1505.1 ± 0.6	1524.6 ± 0.5	1544.0 ± 0.5	1563.8 ± 0.3
1,2,3,5-Tetramethylbenzene	1129.0 ± 0.1	1137.0 ± 0.1	1146.2 ± 0.8	1153.8 ± 0.35	1456.3 ± 0.3	1474.5 ± 0.2	1491.7 ± 0.3	1508.6 ± 0.8
1,2,4,5-Tetramethylbenzene	1124.7 ± 0.1	1132.4 ± 0.1	1141.4 ± 0.8	1149.0 ± 0.4	1447.3 ± 0.4	1463.0 ± 0.1	1480.3 ± 0.2	1496.8 ± 0.9
1,2,3,4,5-Pentamethylbenzene	1281.8 ± 0.2	1292.6 ± 0.1	1303.6 ± 0.15	1314.7 ± 0.15	1644.5 ± 0.2	1666.7 ± 0.2	1688.0 ± 0.95	1710.9 ± 0.2
1,2,3,4,5,6-Hexamethylbenzene	1483.6 ± 0.1	1452.4 ± 0.1	1465.2 ± 1.0	1480.2 ± 0.47	1838.3 ± 0.4	1866.9 ± 0.4	1894.0 ± 0.5	1922.6 ± 0.6

Table 2
Retention indices of the chlorobenzenes on ZB-WAX

Solute	120 °C[a]	140 °C	160 °C	180 °C
CB	1257.1	1279.1 ± 0.3	1295.0 ± 0.8	1311.3 ± 0.9
1,2-C2B	1529.8	1548.7 ± 0.2	1570.2 ± 0.2	1592.6 ± 0.6
1,3-C2B	1455.4	1474.1 ± 0.4	1494.6 ± 0.6	1513.3 ± 0.7
1,4-C2B	1483.2	1500.8 ± 0.5	1519.6 ± 0.3	1538.8 ± 0.6
1,2,3-C3B	1743.2	1768.6 ± 0.2	1795.3 ± 0.2	1822.1 ± 0.3
1,2,4-C3B	1665.5	1688.6 ± 0.3	1710.4 ± 0.7	1735.8 ± 0.4
1,3,5-C3B	1550.0	1569.3 ± 0.2	1589.5 ± 0.3	1610.7 ± 0.6
1,2,3,4-C4B	1914.1	1938.0 ± 0.4	1968.2 ± 0.3	2001.1 ± 0.4
1,2,3,5-C4B	1790.6	1823.7 ± 0.2	1850.3 ± 0.2	1876.9 ± 0.4
1,2,4,5-C4B	1801.8	1815.4 ± 0.2	1842.5 ± 0.2	1869.6 ± 0.1
1,2,3,4,5-C5B	1998.1	2026.2 ± 0.1	2059.8 ± 0.1	2093.5 ± 0.2
1,2,3,4,5,6-C6B	2153.0	2202.3 ± 0.3	2243.1 ± 0.3	2284.0 ± 0.4

[a] Calculated with the *k* values obtained by the extrapolation of lnk vs. *T*. CB, chlorobenzene; C2B, C3B, C4B, C5B and C6B, dichlorobenzenes, trichlorobenzenes, tetrachlorobenzenes, pentachlorobenzene and hexachlorobenzene.

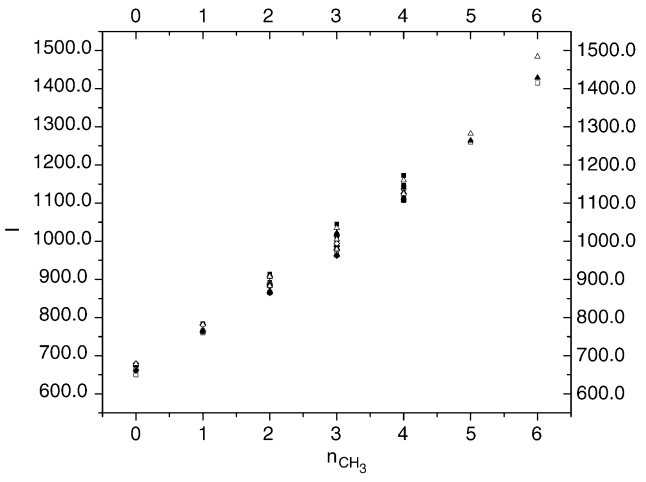

Fig. 2. Comparison of the retention indices of benzene and the 12 methylbenzenes on nonpolar stationary phase at 100 °C. Retention index sources: (■), Apolane-87, ref. [15] (□), squalane, ref. [7] (●), SE-30, ref. [10] (○), OV-101, ref. [11] (♦), DB-1, ref. [12] (◊), DB-5, ref. [12] (▲), PONA, ref. [19] (△), HP-5 this work.

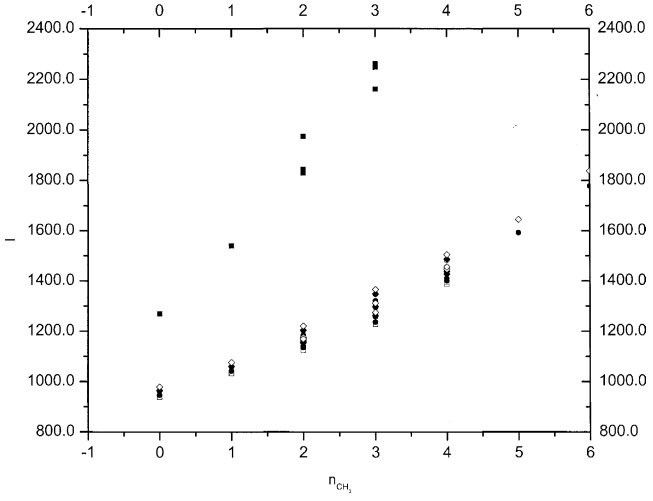

Fig. 3. Comparison of retention indices of benzene and the 12 methylbenzenes on polyethylene glycols Retention index sources: (■), PEG 400, ref. [20] (□), Carbowax 20M, ref. [13] (●), Carbowax 20M, ref. [7] (○), Carbowax 20M, ref [10] (♦), carbowax 1540, ref. [14] (◊), ZB-WAX, this work.

chromatographic conditions. Differences of about 3% are normal and acceptable, because of the column-to-column differences in the composition of the stationary phase materials.

3.1. Retention index temperature effect

Kováts et al. [21] remarked that the relationship between the retention index and the column temperature was not linear: "it can be seen that, in fact, temperature dependence of the retention index is hyperbolic". Therefore, it is admitted that the column temperature dependence is well described by an Antoine-type equation [22–25]:

$$I = A + \frac{B}{C + T} \tag{3}$$

where A, B and C are constants. However, Budahegyi [25] pointed out that this curve can have a significant linear portion, the length of wich depends mainly on the polarity of the solute examined, on the stationary phase applied and on their mutual interactions. This equation was much used in the last century, but recently [26–29] a new equation derived from the application of the kinetic model to the retention indices [27] has been proposed:

$$I = A + \frac{B}{T} + C \ln T \tag{4}$$

It is opportune at this stage to state that over certain temperature ranges the linearity is also a good choice [17].

Table 3 lists the comparison of the linear and non linear temperature dependences of the retention index of benzene and the methylbenzenes on HP-5 and ZB-WAX, respectively. By linear fit we understand the application of the equation:

$$I = A + BT \tag{5}$$

By non linear fit we understand both the application of Eq. (4) and of the squares regression:

$$I = A1 + B1T + B2T^2 \tag{6}$$

For the above analytes we can see that the linear dependence of Eq. (5) is sufficiently good to describe the retention index temperature effect at 373–433 K, although the correlation coefficients obtained with Eq. (4) are slightly better than those obtained with the linear regression.

Table 4 shows the comparison of the fit of the retention index of the chlorobenzenes on HP-5 [17] at the temperature range 373–433 K and of the fit of retention indices of the chlorobenzenes on ZB-WAX at 393–453 K. The retention indices of both species methylbenzenes and chlorobenzenes increase with increasing temperature in all cases.

The linear fit is not good for chlorobenzenes on HP-5, and the 2nd degree polynomial [Eq. (6)] was used for the com-

Table 3
Temperature dependence of the retention indices of benzene and the methylbenzenes

Column	Solute	Eq. (5)[a]			Eq. (4)[b]			
		A	*B*	*R*	*A*	*B*	*C*	*R*
HP-5	B	582.5	0.257	0.991	−4379.8	255120.9	738.8	0.997
	MB	682.2	0.267	0.9867	−3808.6	25120.9	672.5	0.991
	1,2-M2B	776.8	0.352	0.9994	−417.1	226985.2	211.2	0.9995
	1,3-M2B	774.1	0.291	0.9976	117.8	4100.6	127.3	0.998
	1,4-M2B	775.0	0.288	0.9901	−5027.5	299989.2	862.4	0.997
	1,2,3-M3B	874.0	0.433	0.9989	−796.9	46004.8	288.6	0.999
	1,2,4-M3B	873.2	0.354	0.9998	−1688.0	106045	406.8	1.000
	1,3,5-M3B	873.3	0.284	0.9998	−949.1	71916.6	293.1	0.9997
	1,2,3,4-M4B	975.9	0.493	0.9999	−2144.8	120459.8	498.5	1.000
	1,2,3,5-M4B	978.0	0.418	0.9994	−556.3	39559.6	266.7	0.9995
	1,2,4,5-M4B	971.6	0.410	0.9995	−937.9	62377.6	320.1	0.9995
	1,2,3,4,5-M5B	1077.0	0.549	0.99998	−1995.8	113108.8	502.3	1.000
	1,2,3,4,5,6-M6B	1181.8	0.688	0.9996	−3744.1	203379.6	783.2	0.9995
ZB-WAX	B	784.6	0.521	0.9991	−4172.6	224646.2	768.3	0.9999
	MB	863.2	0.573	0.9993	−4412.4	236731.7	819.9	0.9999
	1,2-M2B	964.1	0.688	0.9999	−2818.3	137816.7	619.7	0.99995
	1,3-M2B	949.8	0.607	0.99989	−3121.2	163789	651.6	0.999995
	1,4-M2B	946.4	0.597	0.99959	−3154.5	166525.3	654.8	0.999995
	1,2,3-M3B	1050.9	0.845	0.99998	−3352.0	154978.9	726.6	0.9996
	1,2,4-M3B	1043.4	0.721	0.99993	−2044.2	94120.5	524.2	0.99996
	1,3,5-M3B	1038.5	0.634	0.99981	−2087.2	106273.5	519.7	0.9998
	1,2,3,4-M4B	1140.4	0.977	0.99999	−6985.0	181435.4	845.0	0.999995
	1,2,3,5-M4B	1132.1	0.870	0.99986	−1209.1	33952.2	434.7	0.999995
	1,2,4,5-M4B	1137.6	0.829	0.99983	−4078.4	203706.7	840.9	0.99990
	1,2,3,4,5-M5B	1233.7	1.101	0.99991	−5084.5	235602.3	1029.7	0.99993
	1,2,3,4,5,6-M6B	1316.5	1.399	0.99994	−5502.9	229945.1	1135.6	0.99993

[a] $I = A + BT$.
[b] $I = A + B/T + C \ln T$ (ref. [28]).

Table 4
Temperature dependence of the retention indices of chlorobenzenes

Column	Solute	Eq. (6)[a]				Eq. (5)[c]			Eq. (4)[b]			
		A	*B*1	*B*2	R^2	*A*	*B*	*R*	*A*	*B*	*C*	R^2
HP-5 [17]	CB	−1078.6	8.600	−0.0094	0.9902				21115.1	−1313928	−2831.9	0.9920
	1,2-C2B	413.0	2.637	−0.0025	0.9887				4139.5	−262910	−403.0	0.9880
	1,3-C2B	591.2	1.665	−0.0014	0.9618				2699.2	−168006	−209.0	0.9626
	1,4-C2B	838.2	0.504	0	0.9899				−8388.1	487889	1370.0	0.9986
	1,2,3-C3B	−517.1	7.358	−0.0076	0.9858				14227.5	−924229	−1785.9	0.9845
	1,2,4-C3B	−116.35	5.880	−0.0064	0.9826				14641.4	−869582	−1879.8	0.9797
	1,3,5-C3B	914.9	0.607	0	0.9954				−54.9	−19419	210.5	0.9961
	1,2,3,4-C4B	133.2	5.325	−0.0054	0.9905				3051.5	−212880	−188.2	0.99996
	1,2,3,5-C4B	207.0	4.793	−0.0049	0.9961				9653.8	−598673	−1137.1	0.9955
	1,2,4,5-C4B	1064.7	0.708	0	0.9992				−92.1	−21046	249.1	0.99982
	1,2,3,4,5-C5B	2437.6	−5.276	0.0074	0.9918				−23583.9	1348401	3626.8	0.9834
	1,2,3,4,5,6-C6B	1145.4	1.347	0	0.9833				−28433.9	1598577	4359.8	0.9973
ZB-WAX	CB					907.9	0.893	0.9968	1212.5	44.7	62.7	0.9991
	1,2-C2B					1116.5	1.049	0.9993	1425.9	104.0	101.0	0.9993
	1,3-C2B					1073.5	0.971	0.9998	1371.9	83.5	86.7	0.9999
	1,4-C2B					1118.1	0.928	0.9998	1398.5	84.8	85.5	0.9994
	1,2,3-C3B					1225.7	1.316	0.9999	1626.5	116.8	119.5	0.9995
	1,2,4-C3B					1207.7	1.164	0.9995	1562.2	103.4	105.7	0.9983
	1,3,5-C3B					1152.0	1.012	0.9997	1457.5	92.7	93.3	0.9992
	1,2,3,4-C4B					1339.0	1.457	0.9975	1751.1	163.2	150.1	0.9991
	1,2,3,5-C4B					1231.7	1.427	0.9984	1705.1	85.6	107.8	0.9993
	1,2,4,5-C4B					1345.0	1.153	0.9899	1708.8	92.9	99.6	0.9996
	1,2,3,4,5-C5B					1367.9	1.599	0.9991	1836.7	161.5	155.5	0.9996
	1,2,3,4,5,6-C6B					1303.5	2.168	0.9988	2015.5	137.8	167.8	0.9993

[a] $I = A + B1T + B2T^2$.
[b] $I = A + B/T + C \ln T$ (ref. [28]).
[c] $I = A + BT$.

parison with the fit to Eq. (4). On the contrary, good linear fits are obtained for the some solutes on the polyethylene glycol. We see in the former case the advantage of the utilization of Eq. (6).

Looking at Table 4 one coud not establish the same conclusions, because the second degree fit works better than the fit of Eq. (4) in many cases. It is seen that the retention indices for MBs can be fitted to a straight line in the temperature ranges in which the *I* values are determined, although the *I* can be somewhat better fitted with Eq. (4).

With respect to the chlorobenzenes on HP-5 [17] the linear fit is not advisable because of their low correlation coefficient. The fit to a 2nd degree curve gives a performance comparable to that obtained with Eq. (4), but on ZB-WAX, although the linear fit works good, in many instances the parabolic fit is better enough to describe the *I* temperature dependence.

It is remarkable that benzene and toluene show good linear fits and also good fits wit Eq. (4), on the contrary to the aldehydes and ketones studied in the same conditions on DB-1 and DB-5 over the temperature range 313–423 K [28].

3.2. The effect of the substituents number on the retention index

The retention indices of methylbenzenes (MBs) and chlorobenzenes (CBs) at each temperature increase with the extent of the substitution, i.e., with increasing methyl or chlorine number, n_{CH_3} or n_{cl}. Table 5 gives the results of the sixteen linear (Eq. (5)) and nonlinear (Eq. (6)) regressions (parabolic, square or second degree polynomial) of MBs and CBs on HP-5 and ZB-WAX.

Constant *A* is the independent term of the linear regression; *A*1 is the independent term for the squares regression, *B* and *B*1 are the terms of first degree, and *B*2 the second degree term.

Coefficients *A* and *B* increase with increasing temperature for the 16 linear fits. Correlation coefficients are better for HP-5 as compared with ZB-WAX, irrespective of the identity of the substituent. This trend holds for the *A*1 well. The worst correlation coefficients are for CBs on ZB-WAX. It seems that there is no difference between linear and square fits for the regression of *I* versus the number of of substituents at the *T* intervals studied (Table 5).

3.3. Effect of the substituent chemical nature on the benzene molecule: the methylbenzene/chlorobenzene correspondence

To check the effect of the substituent chemical nature onto the benzene molecule the retention indices of MBs on HP-5 and on ZB-WAX at 100, 120, 140 and 160 °C (Table 1) are compared with the retention indices of CBs on HP-5 at 120–180 °C [17] and on ZB-WAX at 120,140,160 and 180 °C (Table 2).

Table 5
Effect of the number of substituents on the retention index of methylbenzenes and chlorobenzenes at several temperatures

	T (K)	$I = An_{CH_3} + B$			$I = A1 + B1n_{CH_3} + B2(n_{CH_3})^2$					T (K)	$I = An_{cl} + B$			$I = A1 + B1n_{cl} + B2(n_{cl})^2$			
		A	B	R	$A1$	$B1$	$B2$	R			A	B	R	$A1$	$B1$	$B2$	R
MBs on HP-5	373	125.6	645.6	0.993	689.3	81.2	8.1	0.997	CBs on HP-5	393	161.5	710.0	0.995	697.3	170.1	−1.24	0.995
	393	127.0	648.7	0.993	687.6	91.3	5.9	0.997		413	162.3	718.9	0.996	730.5	154.3	1.15	0.996
	413	128.6	651.8	0.992	691.0	92.6	6.0	0.997		433	165.7	725.0	0.995	730.1	162.2	0.50	0.995
	433	129.7	656.6	0.992	699.0	90.8	6.5	0.996		453	170.2	722.9	0.995	752.2	150.2	2.87	0.996
MBs on ZB-WAX	373	142.3	917.0	0.985	982.9	81.8	10.1	0.994	CBs on ZB-WAX	393				1064.0	217.8	−6.1	0.977
	393	145.3	923.4	0.984	992.6	81.8	10.6	0.994		413	175.6	1135.9	0.977	1094.2	208.1	−4.1	0.977
	413	147.9	931.6	0.983	1003.5	82.0	11.0	0.994		433	184.3	1145.9	0.977	1109.3	209.3	−3.6	0.977
	433	158.7	939.3	0.976	1015.2	81.1	11.6	0.993		453	189.4	1156.1	0.976	1122.9	211.8	−5.3	0.977

To do this the I-increments, ΔI (%), defined as 100[I(CB) − I(MB)]/I(MB), are computed for several compounds of both homologous series at the three common temperatures 120, 140 and 160 °C on the HP-5 stationary phase, yielding: ΔI = 8.4, 10.9 and 11.0% for 1-substitution; ΔI = 16.3, 16.4 and 17.1% for 1,2-disubstitution; ΔI = 18.6, 18.8 and 19.1% for 1,2,4-trisubstitution; ΔI = 18.6, 18.9 and 19.4% for 1,2,4,5-tetrasubstitution; ΔI = 17.1, 16.8 and 18.0% for 1,2,3,4,5-pentasubstitution, and ΔI = 16.0, 15.6 and 16.7% for 1,2,3,4,5,6-hexasubstitution, respectively. A slight increase in the retention index increments with increasing temperature is observed.

At each temperature, e.g., 120 °C, the retention index increments of the respective (1-), (1,3-), (1,2,3-), (1,2,3,4-), (1,2,3,4,5-) and (1,2,3,4,5,6-) methyl and chlorine substitutions are compared, with the following I-increment values: ΔI = 8.4, 15.1, 17.7, 18.5, 17.1 and 14.9%, i.e., the relative I-increment rises from one up to four substituents, but it decreases from five to six substituents, perhaps because the entrance of one more methyl radical or chlorine atom in the molecule of a four-substituted or a five-substituted isomer in the same ring might be hindered by the steric effect.

Next, as for the retention indices of the MBs and CBs on the polar ZB-WAX at 160 °C, according to Tables 1 and 2, the retention index increments rank from I(CB) = 1295 and I(MB) = 1112, with a difference of 183 I-units, i.e., about 16.8% referred to MB, up to I(HCB) = 2243 and I(HMB) = 1923, with a difference of 320 I units, ≈16.6% referred to HMB. Therefore, the situation is very much the same as that found for HP-5.

On the other hand, at 140 and 160 °C, ΔI (%) is 25.5 and 25.8% for 1,2,3,4-substitution; ΔI = 20.6 and 21.0% for 1,3,5-substitution, and ΔI = 24.1 and 24.4%, respectively, etc., which suggests a small temperature effect of the relative increment of MBs respect to CBs. However, there are no significant differences with the previous results on HP-5.

Fig. 4 is the plot of the I-increments of the MBs (monomethylbenzene as standard) at 160 °C, computed from the retention indices on HP-5 and ZB-WAX (Table 1), versus the I-increments for CBs (monochlorobenzene as standard) on HP-5 [17] and on ZB-WAX (Table 2), respectively.

For example, I(1,2-dimethylbenzene) − I(methylbenzene) = 929 − 799 = 130, and I(1,2-dichlorobenzene) − I(monochlorobenzene) = 1088 − 887 = 201, so the coordinates of this point are (201, 130) on HP-5 at 160 °C. Analogously, for ZB-WAX we will have (275, 150) the coordinates for 1,2-dimethylbenzene and 1,2-dichlorobenzene at the same temperature.

Two quasiparallel increasing straight lines are obtained, a better one (slope = 0.845 and R = 0.998) for HP-5, while the parameters for ZB-WAX (slope = 0.92 and R = 0.989) show a poorer correlation.

In addition, it is to be remarked that the points corresponding to the species (1,2-), (1,2,3-) and (1,2,3,4-) appear in the straight line in an upper position than their diisomers (1,3-), (1,4-), triisomers (1,2,4-), (1,3,5-), and tetraisomers (1,2,3,5-), (1,2,4,5-).

3.4. Application of Haken et al.'s retention index increments

Haken et al. [1] determined the retention index increments, i.e., the differences between the Is of the CBs, with n_{cl} > 1, and the I of monochlorobenzene used as reference, $\Delta I = I_{CB} - I_{monochlorobenzene}$, finding similar increases to those observed for the retention indices with temperature and with the degree of the hydrogen atom substitution by Cl atoms. Using this procedure we have computed these increments for our experimental retention indices on chlorobenzenes and methylbenzenes. Obviously, for the latter $\Delta I = I_{MB} - I_{toluene}$, where MB means methylbenzenes with $n_{CH_3} > 1$.

In particular, the I-increments at 140 °C of MBs and the homologous CBs on HP-5 and on ZB-WAX are listed in Table 6. Two effects are clearly appreciated: the stationary phase effect and the substituent effect. Referring to the former, for each solute the retention index-increment increases from the nonpolar to the polar stationary phase, e.g., (ΔI(HMB) = 674 on HP-5 against ΔI(HMB) = 795 on ZB-WAX), although the disubstituted meta and para, and 1,3,5-trisubstituted species do not follow the trend: ΔI = 104/101, 102/94 and 200/202, on HP-5/ZB-WAX, respectively, but, rather, the increments are constant. As

Table 6
Incremental retention index differences, ΔI, of the chlorobenzenes and the homologue methylbenzenes [1]

Substituent position	Stationary phase			
	HP-5		ZB-WAX	
	140 °C	140 °C	140 °C	140 °C
	MB	CB	MB	CB
1,2-	132	197	149	270
1,3-	104	159	101	195
1,4-	102	169	94	222
1,2,3-	262	331	301	490
1,2,4-	228	334	242	410
1,3,5-	200	288	202	290
1,2,3,4-	388	543	445	659
1,2,3,5-	355	477	393	545
1,2,4,5-	350	480	381	536
1,2,3,4,5-	513	646	589	747
1,2,3,4,5,6-	674	823	795	923

Reference: 1-substitution. $\Delta I = I_{MB} - I_{monomethylbenzene}$; $\Delta I = I_{CB} - I_{monomethylbenzene}$. MB, methylbenzene's homologous series; CB, chlorobenzene's homologous series.

for the chlorobenzenes, only the 1,3,5-trisubstituted CB does not follow this trend either (ΔI = 288/290). Obviously, the chlorobenzenes show the effect more strongly as compared with the methylbenzenes, because the former have larger retention index increments than the latter.

As for the MBs, it is seen that ΔI(MB) = 132 against ΔI(CB) = 197 for the (1,2-) substitution, and (ΔI(HMB) = 674 compared with ΔI(HCB) = 823 for full substitution on HP-5, while ΔI(MB) = 149 against ΔI(CB) = 270, and ΔI(HMB) = 795 against ΔI(HCB) = 923 for the same substitutions on ZB-WAX. Therefore, the retention index increments increase with the degree of methyl or chlorine replacement in the benzene molecule for all congeners in the two homologous series for the two stationary phases, again showing a stronger effect in the polar stationary phase. Therefore, chlorobenzenes are longer retained than methylbenzenes on both stationary phases. Something already seen previously is also confirmed: the larger values for the (1,2-), (1,2,3-) and (1,2,3,4-) species against the two diisomers (1,3-) and (1,4-), the two triisomers (1,2,4-) and (1,3,5-), and the two tetraisomers (1,2,3,5-) and (1,2,4,5-), as seen in the plot of Fig. 4.

3.5. Application of Macák et al.'s retention index increments

The effect of the hydrogen atom replacement in the benzene molecule's ring by $-CH_3$ groups from one to six sub-

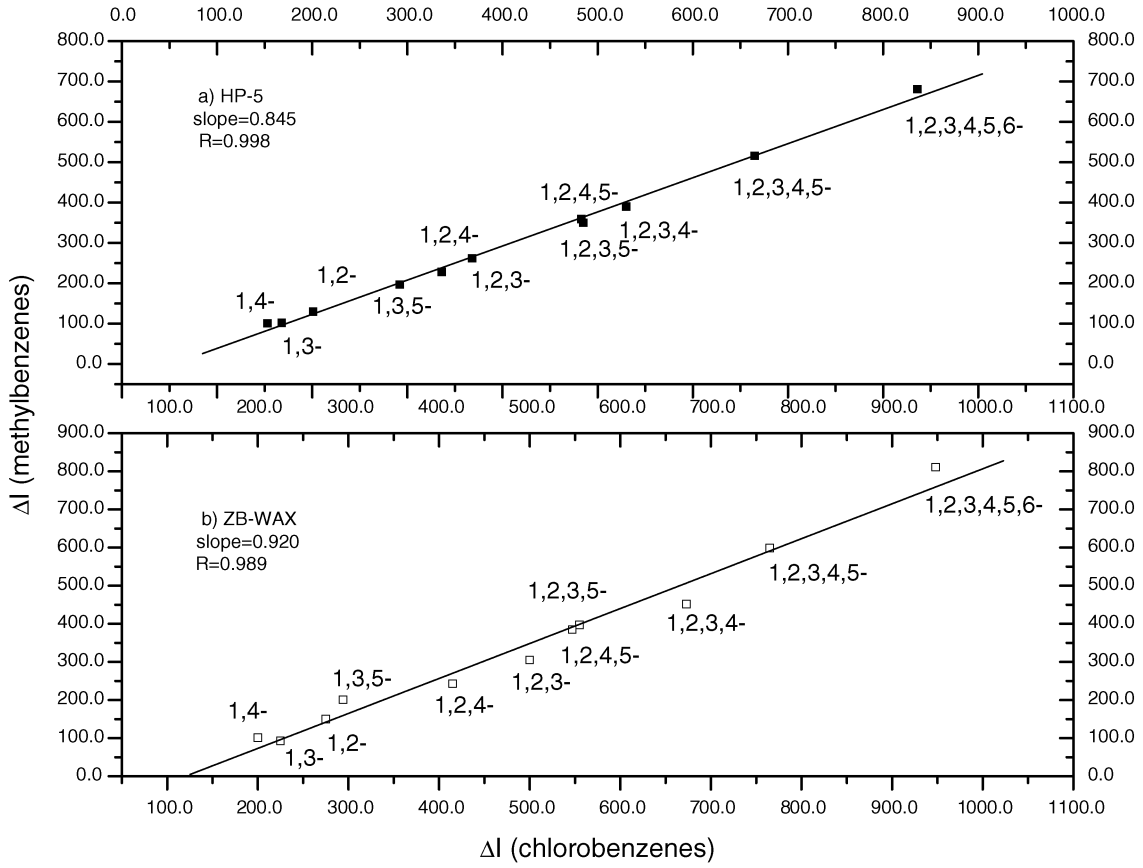

Fig. 4. Plots of the retention index increments of methylbenzenes vs. the retention index increments of chlorobenzenes at 140 °C: (a) HP-5 and (b) ZB-WAX. Solutes: 1, 1,2-X2benzene; 2, 1,3-X2benzene; 3, 1,4-X2benzene; 4, 1,2,3-X3benzene; 5, 1,2,4-X3benzene; 6, 1,3,5-X3benzene; 7, 1,2,3,4-X4benzene; 8, 1,2,3,5-X4benzene; 9, 1,2,4,5-X4benzene; 10, 1,2,3,4,5-X5benzene, and 11, 1,2,3,4,5,6-X6benzene. X, substituent chemical nature: (CH_3 or Cl).

stituents was investigated by Macák et al. [8] on squalane. The calculated retention index increment, δI, of each compound with respect to that from which it stems, e.g., the three disubstituted species 1,2-, 1,3- and 1,4- come from the monosubstituted species. Up to 17 methylbenzenes were computed.

Following this method the increment (or difference) between the retention index values of the same seventeen methylbenzenes and homologue chlorobenzenes and the compounds from which they stems are computed on HP-5 and ZB-WAX at 140 °C.

These I-increments $\delta I = I_2 - I_1$ are listed in Table 7. I_2 is the retention index of a methylbenzene and I_1 the retention index of the parent congener with one less methyl, for instance $\delta I = I$(1,2-M2B) $-$ I(MB), etc. Macák et al. also referred to this increment as δ_{CH_2}.

Fig. 5 is the plot of the I-increments, δ_{CH_2}, of the methylbenzenes on HP-5 and ZB-WAX computed at 100 °C versus the increments δ_{CH_2} of the same 17 compounds obtained by Macák et al. [8] on squalane at 96 °C. The acceptable linearity of the straight lines is shown by the linear regression parameters: slope = 1.228 ± 0.029, intercept = −28.99 ± 3.70, correlation coefficient = 0.9959 on HP-5, and slope = 2.094 ± 0.051, intercept = −121.05 ± 6.55, R = 0.9956 on ZB-WAX, which highlight a good correlation between our results and those of Macáks et al. on methylbenzenes. Comparing the I-increments for chlorobenzenes obtained at 140 °C on ZB-WAX (Table 7) with the δ_{Cl} obtained with the data of Haken et al. [1] on Carbowax 20M at the same temperature a worse linearity (R = 0.907) was obtained, but it still supports the correlation between the results of the retention index increments of the chlorobenzenes on the two polyethylene glycols.

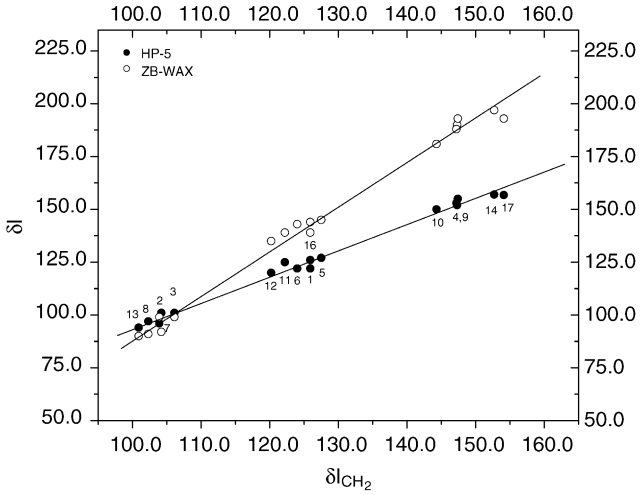

Fig. 5. The retention index increments of methylbenzenes calculated by Macák et al. [8] on squalane, δI_{CH_2}, vs. those calculated by us, δI, on two stationary phases (●), HP-5 and (◯), ZB-WAX). See Table 7 for the identity of the solutes.

3.6. Methylbenzenes

According to Table 7, the δI of the dimethylbenzenes generated from toluene are 132, 104, and 102, on HP-5, and 149, 101 and 94 on ZB-WAX, hinting at the sequence *metha* ≈ *para* < *ortho*. The *ortho* position is the isomer with the highest electronic density, and, subsequently, the introduction of one more methyl will produce a higher I-increment as compared with its other isomers.

As for the five triisomers, the largest I-increment δI = 158/200 (HP-5/ZB-WAX) corresponds to the formation of

Table 7
Retention index increment, δI, of the methylbenzenes and chlorobenzenes relative to their parent compound on two stationary phases

Number	Basic compound before substitution	Basic compound after substitution	Stationary phase			
			HP-5		ZB-WAX	
			Methylbenzenes	Chlorobenzenes	Methylbenzenes	Chlorobenzenes
	Benzene	1	104	191	99.5	279.5
1	1	1,2	132	197	149	270
2	1	1,3	104	159	101	195
3	1	1,4	102	169	94	222
4	1,3	1,2,3	158	172	200	295
5	1,3	1,3,5	96	129	101	95
6	1,2	1,2,3	130	134	152	220
7	1,2	1,2,4	96	137	93	140
8	1,4	1,2,4	126	165	148	188
9	1,2,4	1,2,3,4	160	209	223	249
10	1,2,4	1,2,4,5	122	146	156	126
11	1,2,3	1,2,3,4	126	212	144	169
12	1,2,3	1,2,3,5	93	146	92	88
13	1,3,5	1,2,3,5	155	189	191	255
14	1,2,4,5	1,2,3,4,5	163	166	208	211
15	1,2,3,5	1,2,3,4,5	158	169	196	202
16	1,2,3,4	1,2,3,4,5	125	121	144	88
17	1,2,3,4,5	1,2,3,4,5,6	161	177	206	176

T = 140 °C [8].

1,2,3-M3B by the entrance of a third methyl in the ring between the two vertices of the hexagon occupied by methyls in the *m*-xylene, which is called "double *ortho* effect" [8], i.e. the third methyl enters in an *ortho* position with respect to the already existent methyls. The same isomer generated from *o*-xylene has an smaller δI (130/152) because, although the third methyl enters in an *ortho* position with respect to the two adjacent vertices of the ring, it has an hydrogen atom and a methyl as neighbours, not two methyls as in the previous case. The formation of 1,2,4-M3B from *p*-xylene (δI = 126/148) shows similar increments, and the other two species generated from *m*-xylene and *p*-xylene, respectively, even lower, δI = 96/101 and 96/63, since the third methyl enters the ring in positions far away with respect to the existing methyls, softening the steric effect.

The 1,2,3,4- and 1,2,3,5-tetraisomers generated by the introduction of a fourth methyl in the ring of 1,2,4- and 1,3,5-, respectively, in *ortho* position are the ones with largest *I*-increments (δI = 160/223 and 155/191). On the contrary, 1,2,3,5- generated from 1,2,3- is the one with lowest *I*-increment (δI = 93/92), since the methyl enters in a position far away from the double *ortho* and with hydrogens as the two neighbours, lowering again the steric effect. 1,2,3,4- and 1,2,4,5-, generated from 1,2.3- (δI = 126/144) and 1,2.4- (δI = 122/156), upon introducing the methyl externally to the double *ortho* or *ortho–para* positions, so that it has a methyl and a hydrogen as neighbours, are in an intermediate position.

Pentamethylbenzene formed by the introduction of a fifth methyl in the ring of 1,2,4,5- or 1,2,3,5- are the ones with the largest *I*-increments, δI = 158/196 and 163/208, respectively, because the methyl will enter in an ortho position with respect to the neighbours in the ring. On the contrary, the MB generated from 1,2,3,4-, the one of lowest δI = 125/144, will not.

Hexamethylbenzene has a high *I*-increment, δI = 161/206, because the sixth methyl can only enter the ring in the only possible vacant position, i.e., *ortho* position with respect to the neighbours, one and five vertices, so that there will be a significant *ortho* effect.

3.7. Chlorobenzenes

The extention of Macáks treatment to chlorobenzenes is a contribution of this work. The penetration of a chlorine atom in the benzene molecule produces a larger *I*-increment than that of a methyl group, δI = 191/279 against 104/99.5 (HP-5/ZB-WAX). The sequence increment of dichlorobenzenes is $m < p < o$, with δI = 159/195, 169/222 and 197/270, the isomer with largest retention index increment being the one in the *ortho* position.

The trichlorobenzenes with largest δI are 1,2,3- generated from 1,3- (172/295) by double *ortho* effect and 1,2,4- generated from 1,4- (165/188) by single *ortho* effect, but in the first case the new chlorine has two chlorines as neighbours as compared with one in the second. The species 1,3,5- generated from 1,3- and 1,2,3- from 1,2- have the lowest increments, 129/95, and 137/140, because as the third chlorine enters the ring in positions far away from the other chlorines already present in the parent diisomers, it probably lowers the electronic density, and, therefore, the electrical interaction with the stationary phases.

Similarly, the three tetrachlorobenzenes with largest δI are 1,2,3,4- from 1,2,4- (209/249), 1,2,3,4- from 1,2,3- (212/169), and 1,2,3,5- from 1,3,5- (189/255), the first two because of the double *ortho* effect as the fourth chlorine atom enters the ring in *ortho* positions, while 1,2,4,5- from 1,2.4- (δI = 146/126) and 1,2,3,5. from 1,2.3- (δI = 146/88) are the isomers with smallest increments because the new chlorine enters the ring in positions far away from the *ortho* positions, with a subsequent lowering of the electronic density.

Pentachlorobenzene generated from 1,2,3,4- is the one with smallest δI (121/88) because the fifth chlorine although enters the ring in an *ortho* position, one of their neighbours being hydrogen. The largest δI values are of pentachlorobenzene formed from 1,2,4,5-, (166/211), and from 1,2,3,5- (169/202) due to the quadruple *ortho* effect, since in both cases the fifth chlorine enters the ring in an ortho position with respect to the other four chlorines. Finally, hexachlorobenzene generated from the chlorination of pentachorobenzene has a surprisingly low *I*-increment, $\delta I \approx 177$ for both stationary phases, bearing in mind the strong steric effect of this molecule. Therefore, the trend is similar to that found in methylbenzenes.

4. Conclusions

The retention indices of chlorobenzenes calculated at 120, 140, 160 and 180 °C on HP-5 and at 140, 160 and 180 °C on ZB-WAX (our stationary phases), and those reported in the literature on SE-30 and Carbowax 20M at the same temperature ranges, are in good agreement.

The retention indices of methylbenzenes at 100 °C obtained by us on HP-5 and ZB-WAX agree with data taken from the literature.

The retention indices of MBs and CBs increase with increasing temperature in HP-5 and ZB-WAX, over the temperature ranges 373–433 and 393–453 K. The linear and Eq. (4) [26] fits were compared, with slight advantage of the latter. Correlation coefficients were good, specially on ZB-WAX.

Retention indices of both series of compounds increase with increasing number of substituents, irrespective of their chemical nature. The linear and nonlinear *I* versus substituent number regressions are equivalent. The effect of the chemical function of the benzene derivative is also clear: the retention index of CBs are 16% larger than the retention index of MBs at the different temperatures.

Plots of *I*-increments of MBs versus CBs on both stationary phases, taking the mono-isomer as reference, give increasing straight lines with correlation coefficients of 0.998 and 0.989 on HP-5 and ZB-WAX, respectively.

At a given temperature, the *I*-increments computed as *I*(MBs) − *I*(methylbenzene) and *I*(CBs) − *I*(monochlorobenzene) are larger for the polar stationary phase, and for a given stationary phase, ΔI(MBs) < ΔI(CBs). Both increments increase with increasing substitution in all cases.

The *ortho* position has a larger retention index than their *meta* and *para* homologues; the 1,2,3-substitution has a larger retention index than their 1,2,4- and 1,3,5- homologues, and the 1,2,3,4-substitution has a larger retention index than their 1,2,3,5- and 1,2,4,5-homologues.

A fair agreement is found between the incremental retention index of metylbenzenes and chlorobenzenes obtained by us on HP-5 and ZB-WAX and the results published by Haken et al. [1] on SE-30 and Carbowax 20M, and by Macák et al. [8] on squalane.

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