Behaviour of the isothermal retention indices of *n*-alkylbenzenes on stationary phases of different polarity

José María Santiuste [a,*], Jesús Eduardo Quintanilla-López [b], Jószef M. Takács [c], Rosa Lebrón-Aguilar [a]

[a] *Instituto de Química-Física "Rocasolano" (CSIC), Serrano 119, 28006 Madrid, Spain*
[b] *Instituto de Química Orgánica General (CSIC), Juan de la Cierva 3, 28006 Madrid, Spain*
[c] *Gas Chromatographic Research Group for Study of the Retention Index System, Fábián u. 27, Budapest, Hungary*

ABSTRACT

Isothermal retention indices (I) of benzene, toluene, ethylbenzene, *n*-propylbenzene and *n*-butylbenzene were determined at 323–423 K on twelve WCOT capillary columns covering a broad stationary phase polarity spectrum. These I values have been tested carrying out a comparison with the NIST database values. The effect of the stationary phase polarity on I values was studied. But for the poly(3,3,3-trifluoropropylmethyl siloxane) column, a good linear correlation was found. At each temperature, the dependence on I of the alkyl chain length (z) attached to the ring of the *n*-alkylbenzenes was linear and of similar magnitude for the stationary phases of low to middle polarity, but lower for the more polar ones. Moreover, an important influence of the column temperature on the slope of the I *vs.* z plots was observed for the only non polysiloxane-type stationary phase studied, *i.e.*, poly(ethylene glycol), due to its higher chain stiffness. Finally, different expressions describing the effect of the temperature on the retention index have been compared. I values of the *n*-alkylbenzenes in the 323–423 K range increase with increasing column temperature according to the Antoine-type ($I = \alpha + \beta(\gamma + T)^{-1}$) and the extended ($I = a + bT^{-1} + c \ln T$) models. No significant differences were observed between them, except for the poly[70% *bis*(3-cyanopropyl) 30% dimethyl silphenylene-siloxane] column, for which the Antoine-type model was slightly better.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Isothermal retention indices or Kováts indices are the parameters more widely used in gas chromatography for describing the retention of non-*n*-alkane solutes on the stationary phases [1]. The retention indices (I), devised by Kováts in 1958, a few years after the invention of gas chromatography by James and Martin [2], continue to be a simple yet sound and robust method of characterising solute-phase interactions. Thousands of papers and reviews [3] have been published since then and, fifty three years later, the interest of the subject is far from decaying, the retention index being still actively investigated.

Kováts defined the I of the *n*-alkanes as 100 times its carbon atom number (z), irrespective both of the column temperature and of the nature of the stationary phase [1]. In the same way, he defined the I of an analyte as 100 times the apparent number of carbon atoms of a hypothetical *n*-alkane that would have the same reten-

tion as the analyte under identical chromatographic conditions. In mathematical terms the retention index is:

$$I_i = 100 \left[z + \frac{(\log rm_i - \log rm_z)}{(\log rm_{z+n} - \log rm_z)} \right] \qquad (1)$$

where rm is the chosen retention magnitude, usually the adjusted retention time ($t_{R'}$), retention factor (k), specific retention volume (V_g), *etc.*, and the subscripts z and $z+n$ refer to the *n*-alkanes of z and $z+n$ carbon atoms eluted before and after the analyte i.

This expression has been generalised, and it is accepted that a greater accuracy in the estimation of I is achieved if it is deduced from a plot of the logarithms of the adjusted retention times of *n*-alkanes *vs.* their number of carbon atoms ("semilog plot"). However, deviations from linearity have been reported [4–9], and sound proofs of the non-linearity of the "semilog plot" have been given [10].

It is known that the retention index usually increases with the column temperature [1]. Initially, the I *vs.* T plots investigated were seen to increase either: linearly (Eq. (2)) or according to a hyperbola (or Antoine-type curve) (Eq. (3)) [11–13]:

$$I = m + nT \qquad (2)$$

---

* Corresponding author. Tel.: +34 915619400; fax: +34 915642431.
  E-mail address: santius@iqfr.csic.es (J.M. Santiuste).

$$I = \alpha + \frac{\beta}{\gamma + T} \tag{3}$$

where m and n, and α, β and γ are empirical parameters, but with a thermodynamic meaning [13].

For moderate T ranges, the linear model worked sufficiently well. Later some authors found (especially for the first terms of some compound series) minima in the I vs. T plots of polar solutes on non-polar stationary phases [14–16]. A new so-called extended model was proposed in order to account for this minimum [15]:

$$I = a + \frac{b}{T} + c \ln T \tag{4}$$

where a, b and c are constants.

In this paper, isothermal retention indices of n-alkylbenzenes at different temperatures on stationary phases of wide-ranging polarity are presented. The data obtained was employed to study the dependence of I on polarity and composition of the stationary phase, as well as on the length of the alkyl chain attached to the aromatic ring. A comparison of the different models used to explain the variation of I values with column temperature was also carried out.

2. Experimental

2.1. Apparatus and chromatographic columns

Solutes, commercial WCOT capillary columns (stationary phases) and apparatus used in this work have been described in detail elsewhere [17]. However for the sake of convenience the chemical compositions of the studied stationary phases are listed in Table 1.

2.2. Chromatograms

Mixtures of n-alkanes and n-alkylbenzenes (benzene, toluene, ethylbenzene, n-propylbenzene and n-butylbenzene) were chromatographed isothermally from 323.15 to 423.15 K in increments of 10 K ($\pm$0.1 K) using nitrogen as carrier gas. Moreover, other mixtures of n-alkanes and the McReynolds' probes (benzene, n-butanol, 2-pentanone, 1-nitropropane and pyridine) were also injected at 393.15 K for calculating stationary phase polarity (P). In all cases, the n-alkanes present in the mixtures were chosen in order to bracket the n-alkylbenzenes and McReynolds' probes in the chromatograms. About 0.05 μL of these mixtures were injected in a split ratio of 100:1 at least three times on the 12 commercial chromatographic columns coated with the stationary phases whose chemical compositions, McReynolds' constants and polarities are included in Table 1. Under such conditions, symmetric peaks were obtained for all compounds on all the stationary phases and temperatures, with relative standard deviation of retention times lower than 0.34% except for the TR-CN100 column (<0.84%). Chromatograms were recorded with retention times expressed in hundredths of a minute.

In order to simplify the notation, temperatures have been rounded up throughout the manuscript.

2.3. Mathematical treatment

Retention indices (I) were calculated by the LQG method [18]. Thus, the experimental retention times of all n-alkanes eluted in the same chromatogram were used to calculate the parameters A, B, C and D of Eq. (5) [8,9], and then, the I values of all substances in the chromatogram were deduced from Eq. (6). The hold-up time is not needed for the calculations [18].

$$t_R = A + \exp(B + Cz^D) \tag{5}$$

$$I_i = 100 \sqrt[D]{\frac{[\ln(t_{R(i)} - A)] - B}{C}} \tag{6}$$

The McReynolds' constants (X, Y, Z, U and S) were obtained by subtracting the retention indices of the first five McReynolds' probes (benzene, n-butanol, 2-pentanone, 1-nitropropane and pyridine, respectively) on the stationary phase under study at 393 K, and those in the reference non-polar stationary phase Squalane. The polarity of the stationary phase (P) was calculated as the sum of these five McReynolds' constants [19,20].

As indicators of goodness of the fits, the Fischer's factor, the correlation coefficient adjusted for degree of freedom (R_{adj}) and the standard error of the estimate (s_y), also known as root mean squared error (RMSE), were selected. The s_y is the estimated standard deviation of the residuals (the deviations from the model), and it is used to create prediction limits for new observations. Moreover, in order to detect model inadequacies (trends, outliers, etc.), the plot of the Studentized residuals vs. the independent variable was used. The Studentized residuals are the differences between the observed values and the predicted values when the model is fitted using all observations except one, divided by the estimated standard error. They measure how far away each value is from the fitted model when that model is fitted using all of the data except the point being considered. This fact is important, since a large outlier might otherwise affect the model so much that it would not appear to be unusually far away from the line. A Studentized residual greater than 3 in absolute value corresponds to points which lie more than 3 standard deviations away from the fitted model, and which indicate the possibility of being outliers.

Microsoft Office Excel (Microsoft Corp. Redmond. WA, USA), Microcal Origin 6.0 (OriginLab Corp. Northampton, MA, USA) and Statgraphics Centurion XV program (StatPoint Technologies, Warrenton, VA, USA) were used for data handling, basic calculations, and linear and non-linear regressions.

3. Results and discussion

3.1. Isothermal retention indices

In Table 2 the isothermal retention indices for the five n-alkylbenzenes from 323 to 423 K, with an interval of 10 K, on the 12 WCOT columns ordered by increasing polarity of its stationary phase (P) are given. These I values were calculated by the LQG method (Eqs. (5) and (6)) and they are the average values of at least three injections. The mean standard deviation of all these values was 0.4 i.u. (index units), except for the TR-CN100 column at low temperatures (323–353 K) where it was higher (1.9 i.u.). As a general rule, the I values in Table 2 change twofold, rising with increasing temperature for all the 12 commercial columns examined, and also, with increasing P for each temperature.

The I values obtained were compared with literature values in the NIST database [21] for as many stationary phases (SPs) and temperatures as possible. Unfortunately only TRB-1, TRB-5A and ZB-WAX columns allow such a comparison, because isothermal retention indices for the other nine SPs are lacking in the NIST database. Table 3 summarizes the number of determinations (N), temperature range, and minimum (I_{min}) and maximum (I_{max}) I values included in the NIST for poly(dimethyl siloxane) (PDMS), poly(5% diphenyl 95% dimethyl siloxane) (PMPS5) and poly(ethylene glycol) (PEG) stationary phases. Finally, the last column in Table 3 gives the I values for the five n-alkylbenzenes determined in this work at 383 K. Retention indices from NIST for the three SPs available are reported at 273–473 K, benzene and toluene being the solutes with more determinations. There are close to 550 values for the five arenes in the PDMS columns (TRB-1, HP-1, OV-1, SPB-1, DB-1, etc.). For PMPS5 columns (TRB-5A, RTX-5,

Table 1

Chemical composition, McReynolds' constants and polarity of the twelve commercial chromatographic columns studied.

Column name[a]	Stationary phase chemical composition	McReynolds' constants					Polarity
		X	Y	Z	U	S	
TRB-1	Poly(dimethyl siloxane)	14	50	41	61	37	203
TRB-5A	Poly(5% diphenyl 95% dimethyl siloxane)	30	72	62	96	65	324
TRB-20	Poly(20% diphenyl 80% dimethyl siloxane)	68	106	105	165	128	571
TRB-1301	Poly(6% 3-cyanopropylphenyl 94% dimethyl siloxane)	59	123	116	176	122	596
BP10	Poly(14% 3-cyanopropylphenyl 86% dimethyl siloxane)	79	164	149	224	156	772
TRB-35	Poly(35% diphenyl 65% dimethyl siloxane)	124	152	158	237	205	875
TRB-50	Poly(50% diphenyl 50% dimethyl siloxane)	150	170	180	268	240	1007
VB-210	Poly(3,3,3-trifluoropropylmethyl siloxane)	154	236	374	488	322	1574
TRB-225	Poly(50% 3-cyanopropylphenyl 50% dimethyl siloxane)	234	372	343	499	395	1843
ZB-WAX	Poly(ethylene glycol)	340	557	380	595	530	2403
BPX70	Poly[70% bis(3-cyanopropyl) 30% dimethyl silphenylene-siloxane]	413	616	555	791	662	3037
TR-CN100	Poly[bis(3-cyanopropyl) siloxane]	517	742	648	918	784	3608

[a] See [17] for more details of these chromatographic columns.

HP-5, SE-54, *etc.*), there are 51 values, but no determinations for *n*-propylbenzene nor *n*-butylbenzene are available. In the case of PEG columns (ZB-WAX, DB-WAX, Carbowax 20M, PEG-4000, *etc.*) as many as 163 determinations of the five solutes are reported. Our experimental *I* values fall in the middle of the retention index range in all cases. Concordances are better visualized in Fig. 1, where our (full circles) and NIST (empty circles) data for benzene and *n*-butylbenzene in the SPs considered are plotted against column temperature. The graphs show a fair agreement between experimental *I* values and those from the literature.

A high dispersion of the *I* values obtained from de NIST database for the PEG polymers (Fig. 1(c) and (e)) is observed. It is important to bear in mind, that in these polar SPs, apart from the partitioning mechanism, adsorption of apolar analytes (as alkanes) may occur at active sites of the support or of the capillary walls, or at the gas–liquid and liquid–solid interfaces [13], introducing a significant source of error. This fact, together with the necessity of working at infinite dilution conditions, is not always taken into account. In our case, symmetric peaks for the studied *n*-alkanes and *n*-alkylbenzenes were obtained, and the film thickness of the PEG stationary phase (0.5 μm) was high enough to minimize the interfacial adsorption contribution to the retention process [22].

3.2. Influence of the stationary phase polarity on I

As indicated above, for a given temperature the *I* values of the *n*-alkylbenzenes increase as the SP becomes more polar, since induction and orientation interactions with the aromatic ring become more important as *P* increases, as shown by the rise of McReynolds' constant values. All the plots of *I* vs. *P* (data not shown) yielded positive-slope straight lines with good fitting characteristics ($R_{adj} = 0.991$–0.992, $F = 611$–715 and $s_y = 19.0$–21.6 at 393 K). The slopes at 393 K drop from 0.145 (benzene) to 0.130 for *n*-butylbenzene as a consequence of the decrease of the
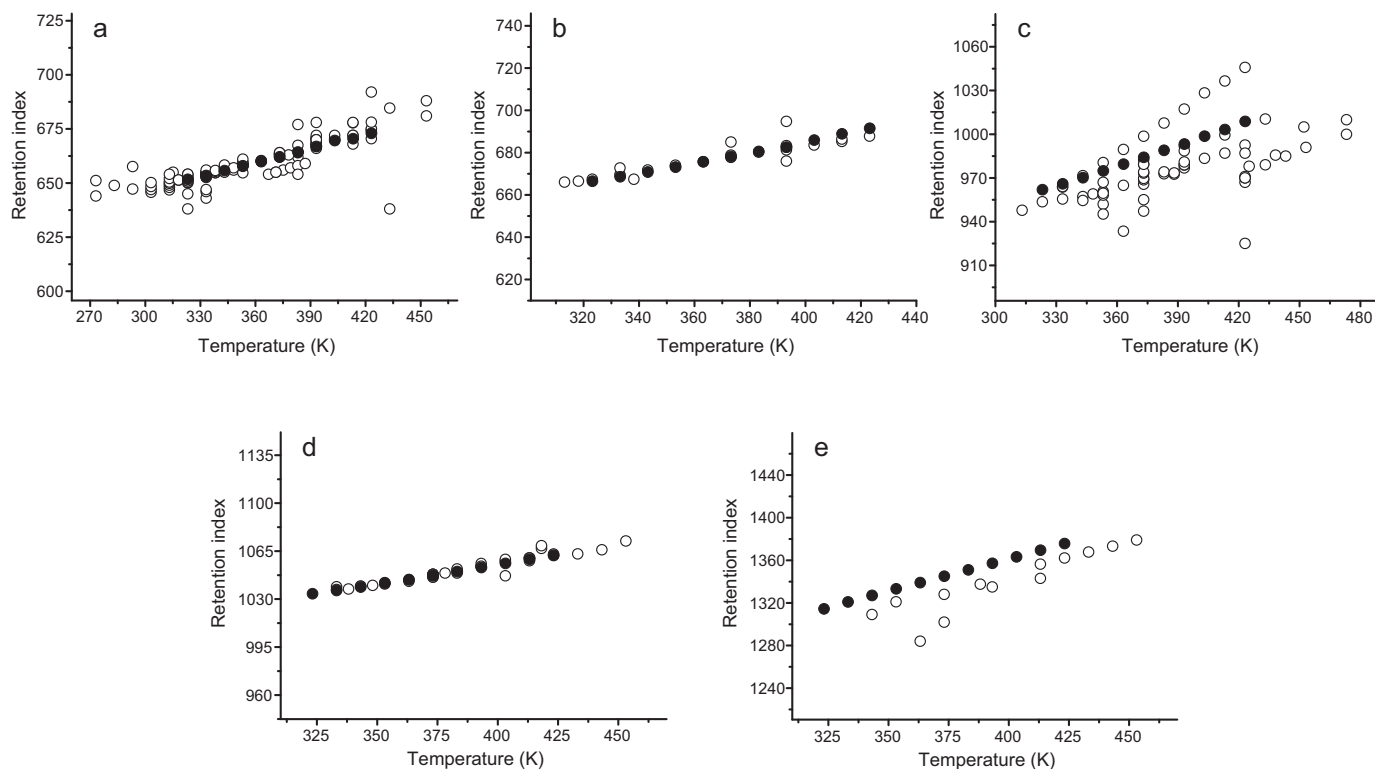

Fig. 1. Comparison between the retention indices of benzene (a–c) and *n*-butylbenzene (d and e) from the NIST database (○) and our experimental values (●) at different temperatures on three types of stationary phases: (a and d) poly(dimethylsiloxanes), (b) poly(5% diphenyl 95% dimethylsiloxanes) and (c and e) poly(ethylene glycols).

Table 2
Retention indices at 323–423 K of *n*-alkylbenzenes on the 12 commercial columns studied.

Column name	Solute	Retention index										
		323 K	333 K	343 K	353 K	363 K	373 K	383 K	393 K	403 K	413 K	423 K
TRB-1	Benzene	651.7	653.4	655.7	657.8	659.9	662.1	664.3	666.9	669.6	672.1	674.4
	Toluene	754.2	756.0	758.3	760.5	763.0	765.2	767.5	770.0	772.6	775.4	777.9
	Ethylbenzene	845.5	847.7	850.1	852.7	855.2	857.8	860.4	863.2	866.0	868.7	871.1
	n-Propylbenzene	935.2	937.5	940.0	942.8	945.5	948.2	951.0	954.1	957.0	959.7	962.4
	n-Butylbenzene	1033.9	1036.2	1038.8	1041.7	1044.3	1047.1	1050.1	1053.0	1056.0	1059.1	1061.9
TRB5-A	Benzene	666.4	668.5	670.8	673.1	675.7	678.1	680.5	683.1	685.9	688.9	691.5
	Toluene	769.2	771.3	773.8	776.2	778.7	781.2	783.7	786.5	789.4	791.9	794.2
	Ethylbenzene	860.9	863.5	866.0	868.7	871.4	874.2	877.0	879.9	883.0	885.9	888.7
	n-Propylbenzene	950.3	953.0	955.7	958.4	961.4	964.4	967.4	970.4	973.6	976.6	979.9
	n-Butylbenzene	1049.4	1052.1	1054.9	1057.7	1060.7	1063.7	1066.8	1070.0	1073.0	1076.2	1079.4
TRB-20	Benzene	702.0	704.1	706.6	709.0	711.5	714.6	717.9	720.6	723.9	727.9	730.6
	Toluene	803.8	806.4	809.1	811.8	815.2	817.8	820.7	824.2	827.3	830.6	833.6
	Ethylbenzene	897.5	900.4	903.3	906.2	909.6	912.5	915.7	919.1	922.6	925.9	929.5
	n-Propylbenzene	986.2	989.0	992.1	995.2	998.7	1001.9	1005.3	1008.7	1012.4	1016.0	1019.5
	n-Butylbenzene	1085.6	1088.5	1091.7	1094.9	1098.2	1101.6	1105.1	1108.5	1112.2	1115.9	1119.6
TRB-1301	Benzene	695.2	697.4	699.6	702.5	704.8	707.1	709.8	712.3	715.4	717.9	721.6
	Toluene	797.8	800.2	802.7	805.2	808.0	810.7	813.3	816.2	819.5	821.7	825.2
	Ethylbenzene	889.7	892.4	895.2	897.9	900.8	903.9	906.8	909.7	912.7	915.9	918.8
	n-Propylbenzene	978.6	981.4	984.2	987.1	990.2	993.5	996.5	999.8	1003.1	1006.5	1009.8
	n-Butylbenzene	1077.8	1080.7	1083.4	1086.6	1089.7	1092.9	1096.1	1099.6	1102.8	1106.2	1109.7
BP10	Benzene	711.5	714.3	717.3	719.8	722.7	725.5	728.6	731.6	734.8	738.2	741.2
	Toluene	814.5	817.3	820.2	822.9	825.9	829.1	832.2	835.4	838.7	841.9	845.2
	Ethylbenzene	906.3	909.3	912.4	915.4	918.7	921.9	925.3	928.7	932.2	935.3	939.1
	n-Propylbenzene	994.8	998.1	1001.3	1004.5	1007.8	1011.3	1014.7	1018.3	1021.9	1025.9	1029.6
	n-Butylbenzene	1094.2	1097.5	1100.9	1104.2	1107.6	1111.0	1114.6	1118.2	1121.9	1125.8	1129.7
TRB-35	Benzene	755.0	757.4	760.7	763.6	766.8	770.5	774.3	777.1	780.7	784.2	788.9
	Toluene	856.6	859.7	863.0	866.3	869.8	873.4	876.9	881.2	884.9	889.2	893.6
	Ethylbenzene	952.4	955.8	959.3	962.7	966.3	970.2	974.1	978.4	982.7	986.4	990.6
	n-Propylbenzene	1039.9	1043.4	1047.0	1050.5	1054.4	1058.2	1062.4	1066.8	1070.8	1075.4	1079.9
	n-Butylbenzene	1139.5	1142.9	1146.7	1150.2	1154.2	1158.1	1162.3	1166.6	1171.1	1175.4	1180.0
TRB-50	Benzene	778.9	781.9	785.0	788.4	791.8	795.3	798.5	803.1	807.0	812.5	817.5
	Toluene	880.2	883.7	887.1	890.7	894.5	898.3	901.8	906.3	910.4	914.6	919.2
	Ethylbenzene	977.0	980.7	984.2	988.2	992.1	996.1	1000.1	1004.3	1008.8	1014.1	1019.0
	n-Propylbenzene	1064.2	1067.7	1071.5	1075.6	1079.5	1083.6	1087.6	1092.4	1096.6	1102.0	1106.6
	n-Butylbenzene	1163.5	1167.4	1171.1	1175.2	1179.3	1183.5	1187.6	1192.3	1197.2	1201.9	1206.7
VB-210	Benzene	783.0	785.5	788.8	792.7	796.0	799.2	803.6	807.0	811.5	815.2	819.9
	Toluene	892.7	895.4	898.7	902.2	905.2	908.5	912.4	915.5	919.1	923.1	927.1
	Ethylbenzene	979.0	981.9	985.6	989.0	992.5	996.0	999.4	1003.1	1006.7	1011.0	1014.8
	n-Propylbenzene	1067.7	1070.8	1074.5	1078.4	1082.1	1085.7	1089.5	1093.6	1097.2	1101.3	1106.0
	n-Butylbenzene	1168.3	1171.6	1175.4	1179.2	1183.0	1186.9	1190.8	1194.8	1199.2	1203.0	1207.1
TRB-225	Benzene	846.0	850.8	855.9	862.1	867.7	873.0	879.1	886.6	892.8	900.3	906.6
	Toluene	949.4	954.5	960.2	966.1	971.9	977.8	983.9	990.6	996.8	1003.9	1010.2
	Ethylbenzene	1042.0	1047.1	1053.2	1059.2	1065.2	1071.2	1077.4	1084.4	1091.0	1097.5	1103.8
	n-Propylbenzene	1127.3	1132.5	1138.7	1144.7	1150.8	1157.1	1163.4	1170.4	1177.0	1184.2	1190.4
	n-Butylbenzene	1227.4	1232.6	1238.9	1245.0	1251.4	1257.9	1264.3	1271.2	1277.9	1284.8	1291.4
ZB-WAX	Benzene	961.9	965.9	970.1	974.8	979.4	984.1	989.0	993.2	998.7	1003.2	1008.8
	Toluene	1057.1	1062.0	1067.0	1072.1	1077.2	1082.4	1088.0	1092.9	1098.3	1103.9	1109.5
	Ethylbenzene	1139.8	1145.3	1150.7	1156.2	1161.5	1167.1	1172.7	1178.2	1183.8	1189.8	1195.6
	n-Propylbenzene	1217.0	1222.9	1228.6	1234.5	1240.1	1245.9	1251.7	1257.5	1263.5	1269.6	1275.9
	n-Butylbenzene	1314.4	1320.9	1327.0	1333.2	1339.0	1345.0	1351.0	1357.1	1363.2	1369.4	1375.7
BPX70	Benzene	971.1	983.7	996.7	1009.2	1022.5	1035.8	1050.3	1066.1	1080.4	1097.6	1113.3
	Toluene	1068.9	1081.4	1094.4	1106.9	1119.9	1133.8	1148.5	1162.7	1177.7	1194.4	1210.0
	Ethylbenzene	1150.9	1163.7	1176.6	1189.4	1202.7	1216.5	1231.2	1245.9	1261.1	1277.5	1293.9
	n-Propylbenzene	1228.3	1241.2	1253.7	1266.7	1280.1	1293.9	1309.0	1323.3	1338.7	1354.6	1372.1
	n-Butylbenzene	1322.8	1335.7	1348.4	1362.0	1375.3	1389.4	1404.2	1419.4	1434.9	1450.9	1467.4
TR-CN100	Benzene	1032.7	1050.4	1067.0	1086.3	1109.5	1127.8	1148.9	1170.1	1189.1	1211.3	1227.7
	Toluene	1126.9	1144.5	1161.5	1180.2	1202.2	1221.8	1241.7	1262.7	1281.7	1304.1	1321.8
	Ethylbenzene	1207.4	1225.1	1242.5	1260.9	1281.9	1302.1	1321.9	1342.2	1362.3	1385.1	1403.0
	n-Propylbenzene	1278.6	1296.0	1313.6	1331.6	1352.4	1371.9	1391.7	1411.7	1431.8	1454.7	1473.2
	n-Butylbenzene	1368.5	1386.2	1404.0	1422.3	1442.8	1462.5	1482.5	1502.1	1523.0	1546.2	1565.6

dispersive forces as the polarity of SP increases. On the other hand, the intercept increases from benzene (632) to *n*-butylbenzene (1031) showing the contribution to the retention of the alkyl chain attached to the ring.

A closer look at the graphs showed that the *I* values for all *n*-alkylbenzenes in the VB-210 column deviate from the fitted model. As an example, Fig. 2(a) shows the fitted model with the 99.0% confidence limits for benzene at 393 K. The point outside the

Table 3
Comparison between the n-alkylbenzenes retention indices from the NIST database and our experimental values on three stationary phases.

Stationary phase[a]	Solute	NIST					I_{383K} [c]
		N	T range (K)	I_{min} [b]/T (K)	I_{max} [b]/T (K)		
PDMS	Benzene	160	273–453	638/323	692/423		662.1
	Toluene	150	273–453	746/273	788/453		765.2
	Ethylbenzene	131	273–453	835/323	880/453		857.8
	n-Propylbenzene	56	305–453	932.2/313	973/453		948.2
	n-Butylbenzene	50	333–453	1037/333	1072/453		1047.1
PMPS5	Benzene	23	313–423	666.03/313	694.74/393		678.1
	Toluene	27	313–423	767.72/313	797.35/423		781.2
	Ethylbenzene	1	393	879.95/393	879.95/393		874.2
	n-Propylbenzene	0					964.4
	n-Butylbenzene	0					1063.7
PEG	Benzene	65	313–473	925/423	1045.9/423		984.1
	Toluene	37	313–473	1026/423	1142.74/423		1082.4
	Ethylbenzene	26	333–473	1100/423	1210/473		1167.1
	n-Propylbenzene	21	343–473	1190.3/363	1310/473		1245.9
	n-Butylbenzene	14	343–453	1284/363	1379/453		1345.0

[a] PDMS: poly(dimethyl siloxanes) as TRB-1, OV-1, DB-1, SPB-1,OV-101, etc.; PMPS5: poly(5% diphenyl 95% dimethyl siloxanes) similar to TRB-5A, DB-5, SE-54, RTX-5, HP-5, SPB-5, etc.; PEG: poly(ethylene glycols) as ZB-WAX, Carbowax 20M, DB-WAX, PEG-4000, etc.

[b] N: number of data; minimum (I_{min}) and maximum (I_{max}) values of the retention index from the literature, which are not necessarily those at the edges of the temperature range.

[c] This work, in the TRB-1, TRB-5A and ZB-WAX columns at 383 K.

confidence limits corresponds to the VB-210 column. In these cases, the residuals plot is a useful tool for determining whether any outliers exist that should be removed from the data. Fig. 2(b) shows the Studentized residuals for benzene at 393 K in all the
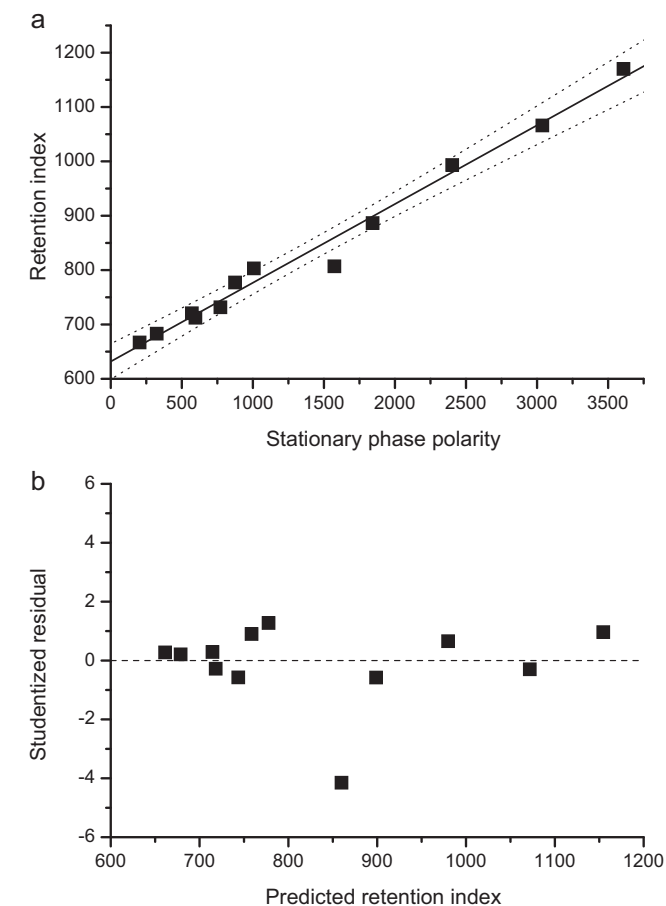

Fig. 2. Dependence of the benzene retention index at 393 K on the polarity of the stationary phase: (a) plot of the fitted model with 99% confidence limits (dotted lines) and (b) residuals plot.

chromatographic columns. As can be seen, the absolute value of the Studentized residual for VB-210 is greater than 3, which indicates the possibility of it being an outlier. This chromatographic column has a poly(3,3,3-trifluoropropylmethyl siloxane) as SP, these polymers having no donor–acceptor interactions with other molecules through n or π electrons (as n-alkylbenzenes) [23], and so its behaviour differs from that of other SPs of similar polarity. This fact is also observed in Table 1, in which the value of the X constant in the VB-210 column is lower than that expected according to its position in the polarity scale. If data from this column are removed from the graphs, the new slopes and intercepts do not change significantly (variation less than 0.3%). However, the fit improves considerably (R_{adj} = 0.996–0.997, F = 1144–1656 and s_y = 12.9–14.2), and no unusual residual is detected.

3.3. Effect of the n-alkylarene chain length on I

The n-alkylbenzenes are low-polarity compounds, with dipole moments close to zero (0–0.6D). If it is assumed that polarity ≈ dipole moment, the polarity may not vary much for the five members of the series. However, changes due to the length of the aliphatic chain attached to the aromatic ring should mark differences in the chromatographic retention and, consequently, in the I values. As electrical properties of the members of a homologous series decrease with increasing chain length, i.e., from benzene to n-butylbenzene, the polar interactions with the SP will also weaken the larger the number of carbon atoms (z) of the alkyl chain. Accordingly, the polarity may be lower for the bulkier elements of the series, say n-propylbenzene and n-butylbenzene, while benzene (no chain) and toluene will be more polar.

Thus, a linear relationship between I and z was found in all instances (different SPs and temperatures), with adjusted correlation coefficients higher than 0.998, Fisher's factors between 1317 and 7962, and standard errors between 3.4 and 7.1. The values of the slopes (q, see Table S1 in Supplementary Data section) are plotted against P in Fig. 3, in which several trends emerge. On the one hand, if only the q data at a single temperature, i.e., 423 K (full points in Fig. 3) are considered, a nearly constant value of q was obtained from low to middle polarities, indicating that for the n-alkylbenzenes dispersion interactions with the SP decrease as much as for the n-alkanes. However, for the most polar SPs (as in ZB-WAX, BPX70 and TR-CN100 columns) lower values of the slopes
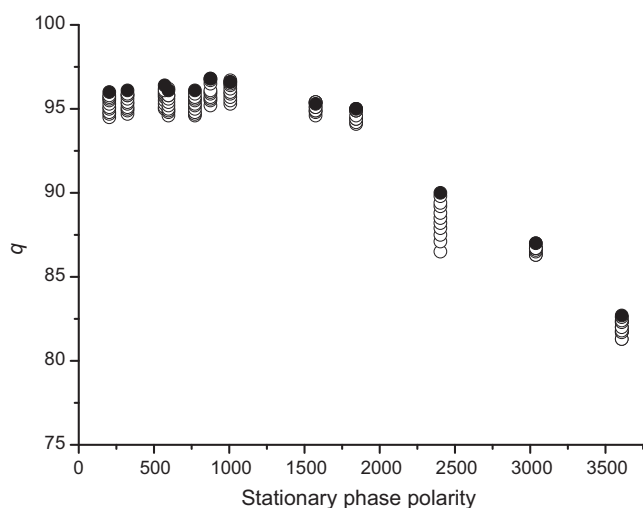
Fig. 3. Variation with the stationary phase polarity of the slopes (q) of the plots of retention index *vs.* the number of carbon atoms (z) of the alkyl chain in the *n*-alkylbenzenes: (●) 423 K and (○) 323–413 K.

were observed. As is well-known, the dispersion interactions are hindered in these very cohesive and polar SPs, causing the retention of the higher *n*-alkylbenzenes to be lower than expected, and hence the increase of I values with z become less pronounced. This behaviour of q values with P was the same for all temperatures studied (empty circles in Fig. 3).

On the other hand, if each SP are separately considered, the q values increase slightly from 0.7 (VB-210 column) to 1.6 (TRB-1301 and TRB-35 columns) in the 323–423 K range. The ZB-WAX column was an exception to this behaviour, since a higher increase of the q value between 323 and 423 K was observed. This quite higher variation of q could be explained bearing in mind that the poly(ethylene glycol) polymers are structurally very different from the polysiloxanes. In fact, the intrinsic properties of the chemical bond Si—O—Si

compared to those of organic C—C—C and C—O—C bonds confer to polysiloxanes not only the flattest bond angles and the longest bond lengths, but also a much higher bond energy and a lower rotation activation energy. Consequently, the polysiloxanes have a unique chain flexibility which allows them a more adaptable orientation of the substituent moieties toward the analytes [20]. These facts lead to a lower temperature effect on the capacity of cavity formation in comparison to the more rigid poly(ethylene glycol) chains.

3.4. Temperature dependence of I

I values for all the *n*-alkylbenzenes studied increase with temperature on all columns tested. Moreover, no minimum was detected for these compounds in the 323–423 K range. Similar results were obtained by Ciazynska-Halarewicz and Kowalska [24] for benzene and toluene on DB-1, DB-5 and DB-Wax columns. The values of Table 2 were fitted to the three models that describe the variation of I with the column temperature, that is, Eqs. (2)–(4). Coefficients and statistical parameters for the fits are summarized in Table S2 in Supplementary Data section. For the sake of clarity, a representative group of the twelve SPs were selected (TRB-1, TRB-35, VB-210, ZB-WAX and TR-CN100), and their fit parameters are given in Table 4.

As for the linear regression (Eq. (2)), slopes and intercepts increase in general with P, and, with z for each SP, except for the most polar columns (BPX70 and TR-CN100), for which a decrease of the intercepts and a high increase of the slopes was observed. Although linear models yielded good fit, a clear trend in their residuals plots was detected, indicating that it is a bad model for explaining the I vs. T variation in the temperature range studied. For the Antoine-type fits (Eq. (3)), the constant α was positive while β and γ were negative, but for *n*-propylbenzene and *n*-butylbenzene in the ZB-WAX column and all the *n*-alkylbenzenes in the TR-CN100 column in which α was negative. In contrast to the linear model, no clear correlation with P or z could be established. It is important to point out that, while good fits were obtained without any trends in their residuals, sometimes the model tended to become unstable,

Table 4

Comparison of different expressions for modelling the retention index variation with column temperature in some representative capillary columns.

| Column name	Solute	$I = m + nT$			$I = \alpha + \beta(\gamma + T)^{-1}$				$I = a + bT^{-1} + c\ln T$			
		m	n	s_y	α	β	γ	s_y	a	b	c	s_y
TRB-1	Benzene	577	0.229	0.39	520	−88,402	−996	0.16	−1141	69,500	273	0.15
	Toluene	676	0.239	0.34	590	−129,074	−1109	0.13	−990	65,784	267	0.14
	Ethylbenzene	761	0.260	0.25	542	−383,373	−1589	0.15	−811	58,716	255	0.11
	n-Propylbenzene	845	0.276	0.27	582	−487,638	−1703	0.18	−796	60,817	267	0.15
	n-Butylbenzene	942	0.283	0.31	766	−279,279	−1368	0.14	−867	69,112	292	0.10
TRB−35	Benzene	645	0.338	0.63	568	−121,662	−975	0.33	−1899	103,065	404	0.34
	Toluene	736	0.369	0.69	679	−102,790	−903	0.12	−2186	120,277	462	0.19
	Ethylbenzene	827	0.384	0.54	679	−221,486	−1134	0.21	−1850	105,674	428	0.17
	n-Propylbenzene	910	0.400	0.64	811	−153,521	−994	0.12	−2069	120,233	474	0.14
	n-Butylbenzene	1007	0.406	0.60	889	−179,478	−1040	0.09	−1937	117,837	469	0.10
VB-210	Benzene	662	0.370	0.75	607	−100,705	−896	0.29	−2318	123,195	471	0.29
	Toluene	781	0.344	0.51	665	−172,788	−1083	0.21	−1623	94,973	384	0.25
	Ethylbenzene	863	0.358	0.40	656	−323,584	−1325	0.18	−1392	85,698	365	0.22
	n-Propylbenzene	944	0.381	0.42	710	−370,589	−1360	0.20	−1441	90,328	386	0.23
	n-Butylbenzene	1041	0.391	0.33	674	−67,4649	−1688	0.15	−1256	84,719	374	0.12
ZB-WAX	Benzene	810	0.468	0.52	527	−446,143	−1350	0.23	−2153	112,729	479	0.24
	Toluene	887	0.524	0.34	219	−142,2790	−2022	0.14	−2004	103,508	474	0.16
	Ethylbenzene	960	0.556	0.26	128	−1,942,210	−2243	0.13	−1912	99,283	475	0.17
	n-Propylbenzene	1028	0.585	0.26	−288	−4,021,760	−2996	0.16	−1913	100,187	488	0.22
	n-Butylbenzene	1118	0.608	0.18	−751	−7,226,570	−3821	0.25	−1532	82,377	449	0.23
TR-CN100	Benzene	385	1.993	2.01	−2355	−6,088,340	−2121	1.94	−10,339	378,893	1765	1.73
	Toluene	483	1.981	1.86	−1663	−4,203,600	−1830	1.49	−10,789	409,383	1843	1.28
	Ethylbenzene	564	1.981	1.93	−1134	−2,996,440	−1604	1.21	−11,316	44,1896	1931	0.99
	n-Propylbenzene	640	1.965	2.05	−594	−1,968,660	−1375	1.00	−11,635	464,581	1986	0.81
	n-Butylbenzene	724	1.983	2.16	−445	−1,836,850	−1336	0.82	−11,954	484,385	2046	0.72
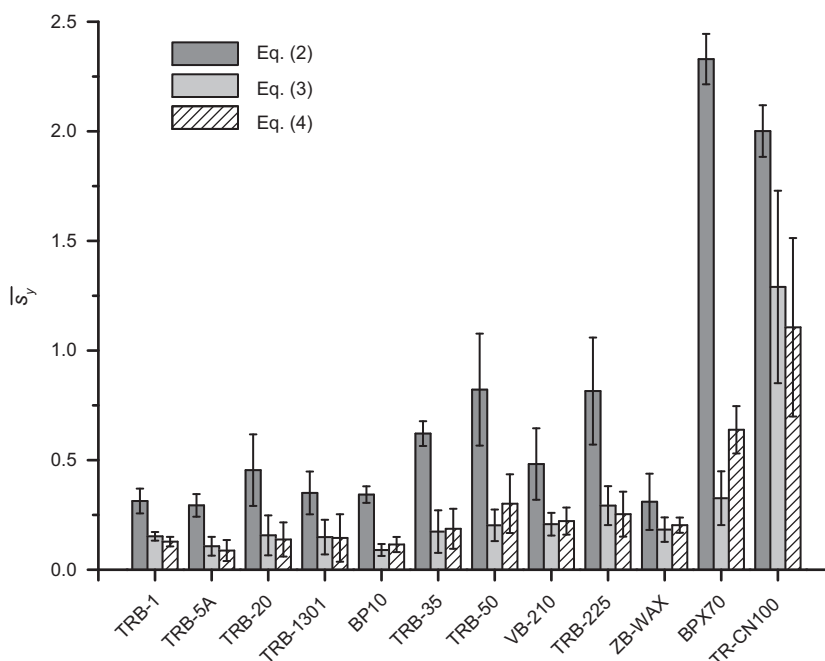
Fig. 4. Comparison of the models used to describe the variation of I vs. T for the n-alkylbenzenes. Whiskers indicate the standard deviation of the mean s_y values.

mainly due to local minimum problems. In such cases, the estimation of the empirical parameters was time-consuming, producing values with a great degree of uncertainty. Regarding the extended model (Eq. (4)), the constant a was negative and the other two positive. Although neither the dependence on P nor on z was clear, values obtained for BPX70 and TR-CN100 columns were higher (in absolute values) than for the rest. Good fits were obtained, without any trend in their residuals plots.

In order to evaluate the best model to describe the I variation of the n-alkylbenzenes in the 323–423 K range, the three different I vs. T fits were compared. As expected for such a large range of temperatures, lower values of s_y were obtained for the non-linear models (see Table 4 and Table S2 in Supplementary Data section). However, it was difficult to ascertain which model (Eq. (3) or Eq. (4)) better describes this variation, since no general rule could be established. As an example, the s_y value for toluene in the TRB-1 column using Eq. (3) is lower than that obtained using Eq. (4), but in the same column the situation for the n-butylbenzene is the opposite. In order to have a global view, the s_y values of the 5 arenes were averaged in each column. The mean s_y values ($\bar{s}_y$) obtained were represented in Fig. 4 for the three equations. As expected, the linear model gave the higher values. However, with respect to models of Eqs. (3) and (4), none of them gave $\bar{s}_y$ values clearly lower than the other. No correlation could be found with the polarity of the SP. Statistical comparison showed that only in one case (BPX70) Eq. (3) was significantly better than Eq. (4). Finally, an overall value was obtained for each model by averaging the $\bar{s}_y$ values for all the columns and compounds. The difference was very small and not significant at the 99% confidence level, i.e., 0.28 ± 0.34 for Eq. (3) and 0.29 ± 0.31 for Eq. (4), and so both models can be considered adequate for describing the effect of temperature on the retention index of n-alkylbenzenes.

4. Conclusions

Isothermal retention indices of five n-alkylbenzenes have been determined by the LQG method on twelve stationary phases of varied polarity between 323 and 423 K. These values were in very good agreement with the NIST database values for poly(dimethyl siloxane), poly(5% diphenyl 95% dimethyl siloxane) and poly(ethylene glycol) stationary phases. However, a higher variability within the NIST data themselves was observed for the poly(ethylene glycol) columns, probably due to neglecting that, in these polar SPs, the I values are greatly affected by the interfacial adsorption and the size of the sample injected.

Linear correlations were found between the n-alkylbenzene retention indices and the polarity of the stationary phase. However, the VB-210 column differed from this behaviour because the poly(3,3,3-trifluoropropylmethyl siloxanes) do not have donor–acceptor interactions with the aromatic ring of the alkylbenzenes. On the other hand, the effect of the alkyl chain length on I was found to be linear and nearly constant from low to middle polarity SPs. For the most polar SPs (ZB-WAX, BPX70 and TR-CN100), lower values of the slopes of I vs. z plot were obtained. Moreover, a significant decrease of these slopes with increasing temperature was observed for the ZB-WAX column, the only one with a non polysiloxane-type polymer as stationary phase. The lower flexibility of their poly(ethylene glycol) chains implies a higher influence of the temperature on the capacity of cavity formation, and, therefore, in the retention of the n-alkylbenzenes.

Finally, the column temperature dependence of I was checked by the linear, Antoine-type and extended models. In the range 323–423 K no significant differences between the use of the two latter models for the 5 arenes studied were found. Only for the BPX70 column, the Antoine-type model was slightly better than the extended one.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chroma.2011.12.007.

References

[1] E.sz. Kováts, Helv. Chim. Acta 41 (1958) 1915.
[2] A.T. James, A.J.P. Martin, Biochem. J. 50 (1952) 679.
[3] G. Tarján, V. Tekler, Sz. Nyredy, S.Y. Mészáros, E. Ullrich, J.M. Takács, in: V. Tekler (Ed.), Retention Indices in Gas–liquid Chromatography (1958–2008), Scientific Society for Organization and Management, Budapest, 2009, p. 7.
[4] L.S. Ettre, Chromatographia 13 (1980) 73.
[5] R.V. Golovnya, D.N. Grigoryeva, Chromatographia 17 (1983) 613.
[6] R.J. Smith, J.K. Haken, M.S.Wainwright, B.G. Madden, J. Chromatogr. 328 (1985) 11.
[7] A. Touabet, M. Maeck, A.Y. Badjah Hadj Ahmed, B.Y. Meklati, Chromatographia 25 (1988) 389.
[8] R. Lebrón-Aguilar, J.E. Quintanilla-López, J.A. García-Domínguez, J. Chromatogr. A 760 (1997) 219.
[9] J.E. Quintanilla-López, R. Lebrón-Aguilar, J.A. García-Domínguez, J. Chromatogr. A 767 (1997) 127.
[10] J.A. García-Domínguez, J.E. Quintanilla-López, R. Lebrón-Aguilar, J. Chromatogr. A 803 (1998) 197.
[11] M.V. Budahegyi, E.R. Lombosi, T.S. Lombosi, S.Y. Mészáros, Sz Nyredy, G. Tarján, I. Timár, J.M. Takács, J. Chromatogr. 271 (1983) 213.
[12] G. Tarján, Sz Nyredy, M. Györ, E.R. Lombosi, T.S. Lombosi, M.V. Budahegyi, S.Y. Mészáros, J.M. Takács, J. Chromatogr. 472 (1989) 1.
[13] V. Pacáková, L. Feltl, Chromatographic Retention Indices – An Aid to Identification of Organic Compounds, Ellis Horwood, Chichester, 1992.
[14] P. Hennig, W. Engewald, Chromatographia 38 (1994) 93.
[15] K. Héberger, M. Görgényi, T. Kowalska, J. Chromatogr. A 973 (2002) 135.
[16] M. Görgényi, K. Héberger, J. Chromatogr. A 985 (2003) 11.
[17] R. Lebrón-Aguilar, J.E. Quintanilla-López, J.M. Santiuste, J. Chromatogr. A 1217 (2010) 7767.
[18] R. Lebrón-Aguilar, J.A. García-Domínguez, J.E. Quintanilla-López, J. Chromatogr. A 805 (1998) 161.
[19] W.O. McReynolds, J. Chromatogr. Sci. 8 (1970) 685.
[20] H. Rotzsche, Stationary Phases in Gas Chromatography, Elsevier, Amsterdam, 1991.
[21] NIST Mass Spec Data Center, S.E. Stein, director, in: P.J. Linstrom, W.G. Mallard (Eds.), NIST Chemistry WebBook, NIST Standard Reference Database Number 69, US National Institute of Standards and Technology (NIST), Gaithersburg, MD, http://webbook.nist.gov (retrieved May 30, and October 4, 2011).
[22] F.R. González, R.C. Castells, A.M. Nardillo, J. Chromatogr. A 927 (2001) 111.
[23] R. Lebrón-Aguilar, J.E. Quintanilla-López, A.M. Tello, J.M. Pérez-Parajón, J.M. Santiuste, J. Chromatogr. A 1100 (2005) 208.
[24] K. Ciazynska-Halarewicz, T. Kowalska, Acta Chromatogr. 13 (2003) 69.