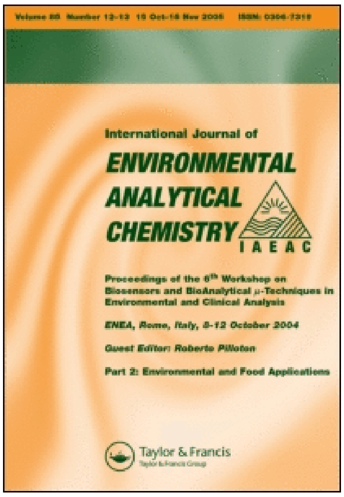

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Analysis of Aromatic Hydrocarbons. Prediction of Gas Chromatographic Retention Indices on Different Stationary Phases and Temperatures

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Analysis of Aromatic Hydrocarbons. Prediction of Gas Chromatographic Retention Indices on Different Stationary Phases and Temperatures

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Relationships between gas-chromatographic retention indices of aromatic hydrocarbons and several parameters were considered. Van der Waals volume was proposed to distinguish the basic skeleton of polycyclic aromatic hydrocarbons. The influence on retention of the stationary phase polarity (p) and column temperature (t) were considered. General equations, I versus t_B and t (t_B=boiling point) and I versus t_B, t and p with high correlation coefficient were obtained. These expressions could be used for analytical purposes.

KEY WORDS: Gas-liquid chromatography; retention index; alkylbenzenes; alkylnaphthalenes; polyaromatic hydrocarbons.

INTRODUCTION

Aromatic hydrocarbons in our environment, as products of incomplete combustion of organic materials and complex industrial products such as naphthas, make their identification and determination an important analytical problem. Gas-liquid chromatography is the most common technique for the analysis of mixtures of aromatic hydrocarbons.

The study of correlations between molecular parameters and retention data makes qualitative evaluation of chromatograms possible. Data prediction of retention indices is important for both theoretical and practical problems, especially when pure standards are unavailable.

Cook and Raushel,[1] Engewald, *et al.*,[2,3] Sojak, *et al.*,[4,5] Tejedor,[6] Papazova and Dimov,[7] Bermejo, *et al.*,[8] Macák, *et al.*,[9] Mészáros, *et al.*[10] have studied retention-structure relationships of alkylbenzenes. Contribution of the aromatic ring and substituents groups, methylene groups increments, stationary phase polarity, temperature variation coefficients and several molecular parameters are considered. Svob, *et al.*[11,12] studied the pyrolysis of alkylbenzenes and identification of the degradation products. Concerning alkylnaphthalenes, the papers of Engewald, *et al.*,[13] Klemm, *et al.*[14] and Gerasimenko, *et al.*[15] may be cited. On retention behavior of polycyclic aromatic hydrocarbons, the works of Lee, *et al.*,[16–18] Wahalen-Pedersen and Jurs,[19] and Lamparczyck, *et al.*[20,21] must be pointed out.

As is well-known, the retention index (I) of a given compound depends upon three attributes: its molecular structure (MS), the stationary phase polarity (p), and the column temperature (t):

$$I = f(MS, p, t) \tag{1}$$

Generally, the works on chromatographic behavior of aromatic hydrocarbons have studied these factors separately. The present authors have proposed general expressions of type:

$$I = f(MS, t) \tag{2}$$

$$I = f(MS, p) \tag{3}$$

applied to several oxygen-containing organic compounds, in previous papers.[22,23]

The aim of this investigation is to obtain general expressions of type (1), (2) and (3) for aromatic hydrocarbons which may be analytically useful for prediction of retention indices in several columns and temperatures.

EXPERIMENTAL

Data and calculations

Table I lists the types of aromatic hydrocarbons, stationary phases and temperatures used in this study. Retention indices of substances were taken from references indicated in this table.

Van der Waals volumes were calculated by the Bondi method[24] amplified by the authors.[25,26] Connectivity indices —*X*— were calculated in accordance with the method of Randić.[27]

RESULTS AND DISCUSSION

Retention index and molecular structure. $I = f(MS)$

One of the molecular parameters used to correlate with I is the connectivity index (X), applied with success by Bermejo, *et al.*,[8] and Kaliszan[28] for alkylbenzenes and polycyclic aromatic hydrocarbons, respectively. Lines I vs. X for aromatic hydrocarbons with different basic skeleton are shown in Figure 1.

If we use Van der Waals volume, a line of better fit is obtained, as can be seen in Figure 2. V_W and X values are listed in Table II. This plot could be interesting to determine analytically the basic skeleton (number and type of rings) of polycyclic hydrocarbons.

These molecular parameters, however, do not distinguish adequately between several positional isomers in alkyl substituted hydrocarbons. Some para-, ortho- and meta-xylenes, for example, present similar X and V_W values and different retention indices. Correlations of retention index (I)-boiling temperature (t_B) were cited previously[12] for homologous series of these compounds (compounds differing in number of $—CH_2—$ groups). Using boiling point, it is possible to distinguish between positional isomers. Figures 3 and 4 show plots of these relationships for alkylbenzenes and alkylnaphthalenes. Table III lists the compounds used to obtain the figures.

It can be observed, that a sudden change in slope appears after *n*-propylbenzene. A similar behavior was observed by Buryan and Macák[29] for the relationship between the logarithm of relative retention and number of carbon atoms of aromatic phenols. Sojåk,

TABLE I
Data set used in the calculations.

Number of compounds	Stationary phase	Stat. phase polarity (p)	Column temperature (t)	Reference
49 Alkylbenzenes	OV-101	7.17	100, 120 and 140°C	15
11 Alkylnaphthalenes	OV-101	7.17	140, 160 and 180°C	15
53 Alkylbenzenes	squalane	0.00	70, 80, 86, 96, 100, 115, 130°C	2, 6, 7, 9
33 Alkylbenzenes	SE-30	6.80	65°C	7
38 Alkylbenzenes	UCON LB 550X	31.19	100°C	6, 7
26 Alkylnaphthalenes	UCON LB 550X	31.19	130°C	13
39 Alkylbenzenes	Carbowax 20M	70.75	100°C	2,7
25 Alkylbenzenes	TCEP	128.91	80°C	7
34 Alkylbenzenes	UCON HB 280X	43.41	100°C	6
26 Alkylnaphthalenes	UCON HB 280X	43.41	130°C	13
27 Alkylnaphthalenes	OV-1	—[a]	130°C	13
10 P.A.H.	SE-30	6.80	250°C	20
10 P.A.H.	OV-101	7.17	250°C	20
10 P.A.H.	SE-52	10.42	250°C	20
10 P.A.H.	OV-7	18.39	250°C	20
10 P.A.H.	OV-17	27.40	250, 270, 290, 310°C	20

[a] Not found in the literature.

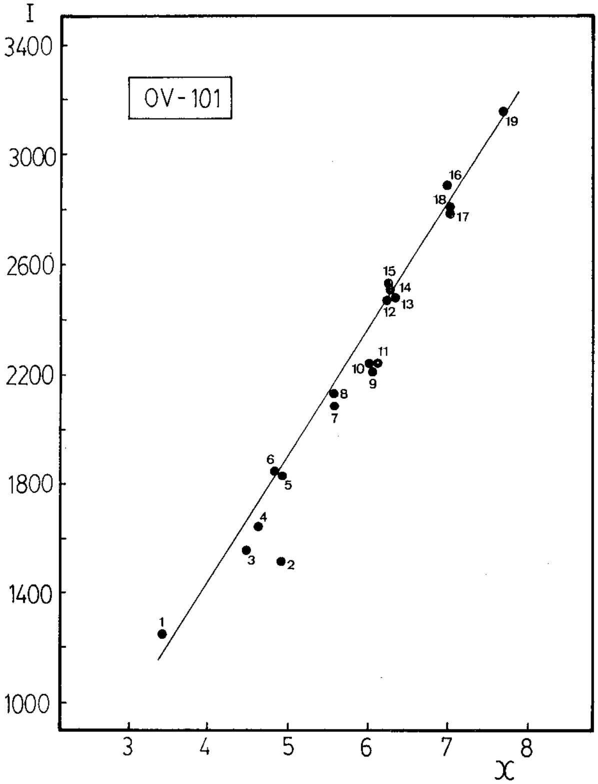


FIGURE 1 Retention Index (I) vs. Connectivity Index (X) for Polyaromatic Hydrocarbons (P.A.H.). (Data from Ref. 28).

et al.[4] also cites an anomalous methylene group increment for *n*-propylbenzene-ethylbenzene.

Equations are: *Alkylbenzenes*

Squalane (96°C)

$I = 3.601\ t_B + 360.772$
(benzene to propylbenzene) (4)
($N = 8$, $r = 0.999$ $s = 2.57$, $F = 8954.06$)

$I = 4.278\ t_B + 254.060$
(propylbenzene to hexylbenzene) (5)
($N = 39$, $r = 0.997$, $s = 4.49$, $F = 8882.70$)

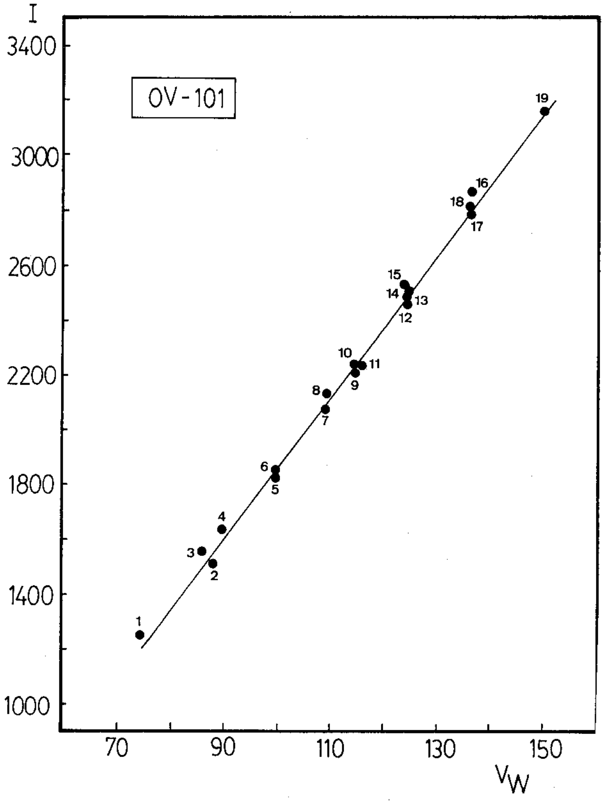


FIGURE 2 Retention Index (I) vs. Van der Waals volume (V_W) for P.A.H. (Data from Ref. 28).

Alkylnaphthalenes

OV-1 (130°C)

$$I = 5.115\, t_B + 58.370 \qquad (6)$$

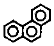
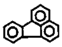
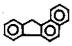
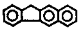
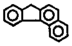
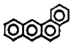
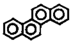
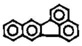
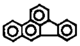
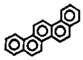
$$(N = 19,\ r = 0.996,\ s = 7.83,\ F = 2246.9)$$

where N = number of experimental points, r = correlation coefficient, s = standard deviation and F = experimental value of Snedecor significance text.

The graphs of these equations have the advantages of including several homologous series that were studied separately by other authors[1,2,6,8] in a single line and the use of an easily available

TABLE II

Retention Index (I), Connectivity Index (X) and Van der Waals Volume (V_W) of P.A.H. (see Figures 1 and 2).

Compound		X	V_W	I (OV-101)
1. Naphthalene		3.405	73.96	1255
2. Acenaphthylene		4.889	87.78	1519
3. Acenaphthene		4.444	86.00	1550
4. Fluorene		4.611	90.00	1645
5. Phenanthrene		4.892	99.56	1836
6. Anthracene		4.809	99.56	1846
7. Fluoranthrene		5.565	109.04	2091
8. Pyrene		5.559	109.04	2139
9. Benzo(a)fluorene		6.022	115.60	2221
10. Benzo(b)fluorene		6.017	115.60	2236
11. Benzo(c)fluorene		6.022	115.60	2236
12. Benzo(c)phenanthrene		6.226	125.16	2464
13. Benzo(ghi)fluoranthrene		6.309	125.16	2473
14. Benzo(a)anthracene		6.220	125.16	2516
15. Chrysene		6.226	125.16	2526
16. Perylene		6.975	134.64	2888
17. Benzo(b)fluoranthrene		6.976	134.64	2795
18. Benzo(j)fluoranthrene		6.970	134.64	2796
19. Picene		7.637	150.76	3159

Van der Waals volume (Fragmentary values): (Ref. 24–26)

=C—H: 8.06 cc mol^{-1}

—CH$_2$—CH$_2$—: 20.46 cc mol^{-1}

=C—: 4.74 cc mol^{+-1}

CH=CH: 18.68 cc mol^{-1}

Aryl—CH$_2$—Aryl: 6.56 cc mol^{-1}

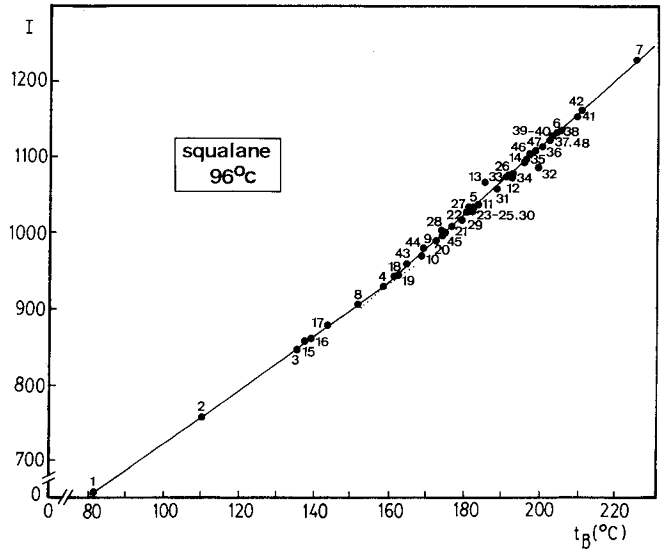


FIGURE 3 Plot I vs. t_B(°C) for alkylbenzenes.

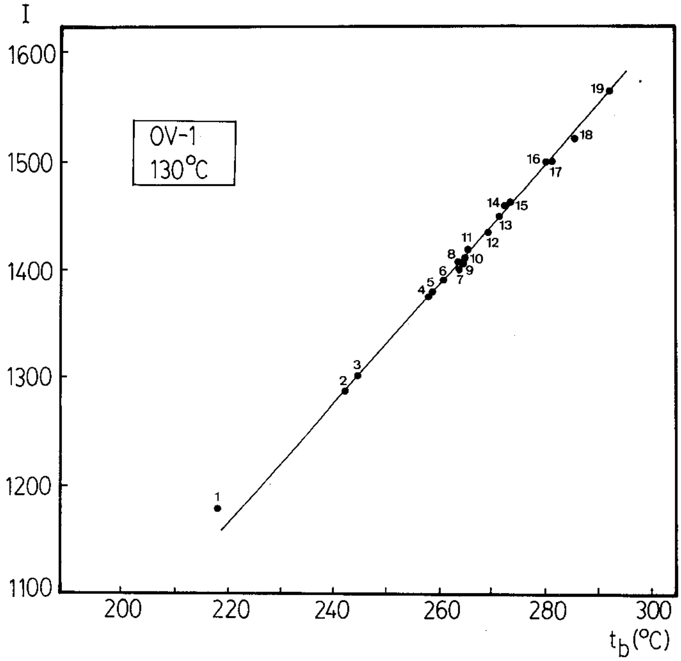


FIGURE 4 Plot I vs. t_B(°C) for alkylnaphthalenes.

TABLE III

Compounds used to obtain Figures 3 and 4.

Alkylbenzenes

Alkylbenzenes

1. B
2. MB
3. EB
4. PB
5. BuB
6. PeB
7. HB
8. iPB
9. iBuB
10. tBuB
11. sBuB
12. sPeB
13. tPeB
14. iPeB
15. 1,4DMB
16. 1,3DMB
17. 1,2DMB
18. 1M3EB
19. 1M4EB
20. 1M2EB
21. 1M4iPB
22. 1M3PB
23. 1M4PB
24. 1,4DEB
25. 1M2PB
26. 1M4tBuB
27. 1,3DEB
28. 1M3iPB
29. 1M2iPB
30. 1,2DEB
31. 1M3tBuB
32. 1M2tBuB
33. 1E3iPB
34. 1E2iPB
35. 1E4iPB
36. 1E3PB
37. 1E2PB
38. 1E4PB
39. 1,3DiPB
40. 1,2DiPB
41. 1,4DiPB
42. 1E4tBuB
43. 1,3,5TMB
44. 1,2,4TMB
45. 1,2,3TMB
46. 1,2,4,5TeMB
47. 1,2,3,5TeMB
48. 1,2,3,4TeMB

Alkylnaphthalenes

1. N
2. 2MN
3. 1MN
4. 2EN
5. 1EN
6. 2,6DMN
7. 2,3DMN
8. 1,6DMN
9. 1,7DMN
10. 1,3DMN
11. 1,4DMN
12. 2iPN
13. 1,8DMN
14. 2PN
15. 1PN
16. 2tBuN
17. 1,3,7TMN
18. 2,3,6TMN
19. 1BuN

B = benzene; N = naphthalene; D = di; T = tri; Te = tetra; M = methyl; E = ethyl; P = propyl; Bu = butyl; Pe = pentyl; H = hexyl; s = sec; i = iso; t = tert.

parameter —t_B—. Other authors[4, 5] also obtained general equations but a large number of empirical parameters were needed.

These equations can be used for prediction of retention indices. Their average relative error is for alkylbenzenes 0.29% and for alkylnaphtalenes 0.39%.

Retention index, molecular structure and column temperature. $I = f\,(MS, t)$

The change of I with temperature is a function of the difference in heats of vaporization—ΔH_v—of a given solute and the *n*-alkanes used as standards. In general the change of ΔH_v with temperature is nearly the same for both compounds, at least over a limited range, as pointed out by Kováts.[30] Plots of I versus t for alkylbenzenes and alkylnaphthalenes are shown in Figures 5 and 6. Mitra and Saha[31] have studied this relationship for many compounds, including aromatic hydrocarbons.

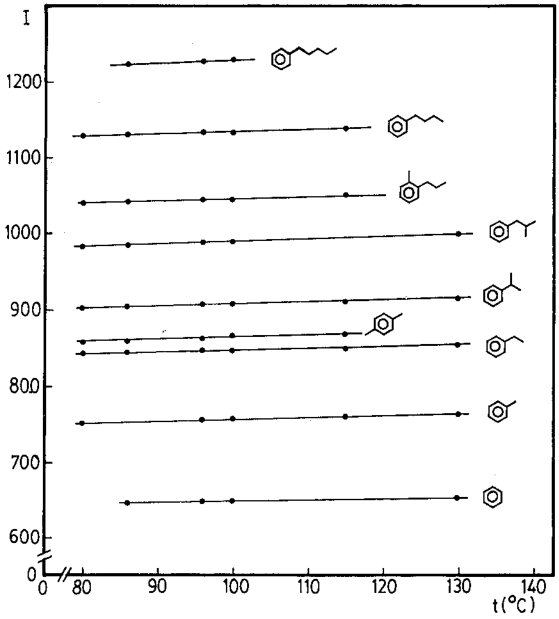


FIGURE 5 Plots *I* vs. column temperature for several alkylbenzenes on squalane.

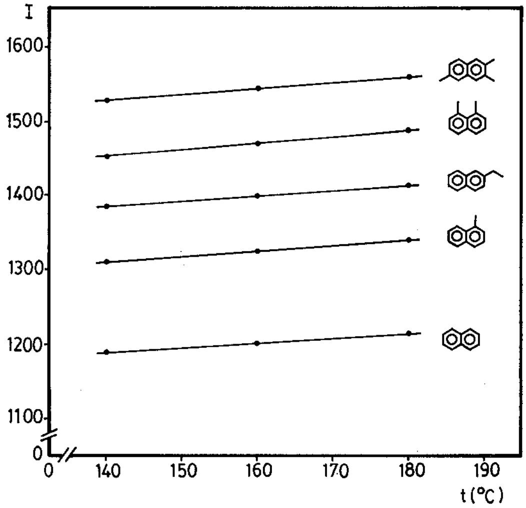


FIGURE 6 Plots *I* vs. column temperature for several alkylnaphthalenes on OV-101.

Expressions with wider application may be obtained if we include molecular structure and column temperature in the same equation; $I=f(MS, t)$. The equations obtained are:

Alkylbenzenes

Squalane

$$I=3.621\ t_B+0.244t+334.261 \tag{7}$$

(benzene to propylbenzene)

$(N=43,\ r=1.000,\ s=2.70,\ F=18793.84)$

$$I=4.282\ t_B+0.315t+222.62 \tag{8}$$

(propylbenzene to hexylbenzene)

$(N=100,\ r=0.998,\ s=3.74,\ F=15714.93)$

Alkylnaphthalenes

(OV-101)

$$I=5.091\ t_B+0.754t-34.559 \tag{9}$$

$(N=33,\ r=0.998,\ s=6.25,\ F=6006.32)$

Polycyclic Aromatic Hydrocarbons

(OV-17)

$$I=6.498\ t_B+1.886t-511.219 \tag{10}$$

$(N=40,\ r=0.995,\ s=48.40,\ F=3449.16)$.

High correlation coefficients and low standard deviations were found in all cases. These equations could be used with analytical purposes for the stationary phase and temperature range indicated. Thus, for example, the average relative error is 0.25% for alkylbenzenes. It must be pointed out that differences of the same order in experimental I values determined in different laboratories may be found in the literature.

Retention index, boiling point, column temperature and stationary phase polarity (p). $I=f(t_B, t, p)$

Figure 7 shows that retention indices of aromatic hydrocarbons increase linearly with the polarity of stationary phase (p). p values were calculated by Tarján, *et al.*[32] and are based on McReynold's system[33]. Retention indices of alkylbenzenes were taken from McReynold's data.[34]

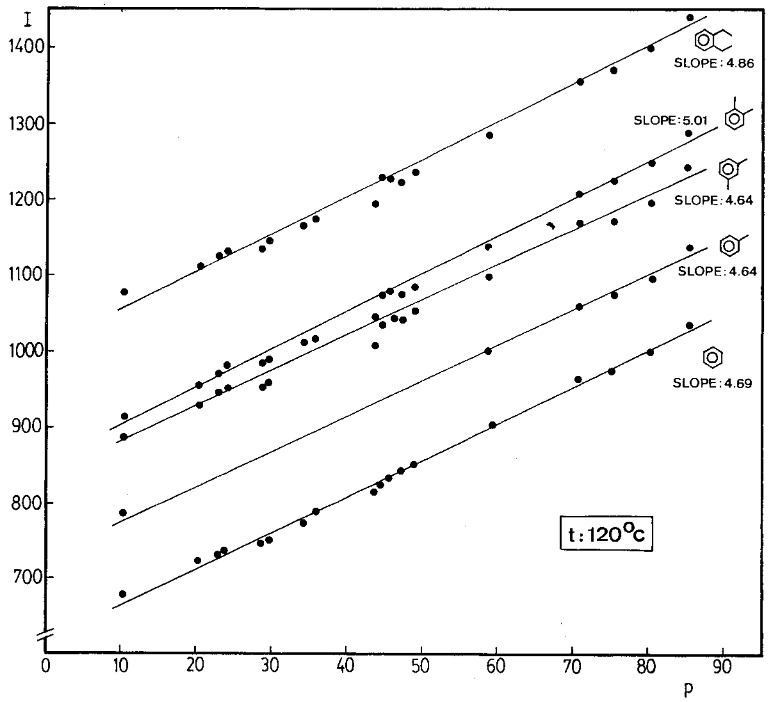


FIGURE 7 Plots I vs. stationary phase polarity for several alkylbenzenes.

The expression with widest application could be obtained if p values were included in the above equations (1)–(10): $I = f(t_B, t, p)$. Thus the equations obtained for alkylbenzenes and alkylnaphtalenes are:

Alkylbenzenes

$$I = 3.948\, t_B + 0.217t + 3.732p + 287.775 \qquad (11)$$
$$(N = 468,\ r = 0.992,\ s = 18.05,\ F = 30246.20)$$

(This expression includes all alkylbenzenes)

Alkylnaphthalenes

$$I = 6.001t_B + 4.854t + 9.333p - 959.658 \qquad (12)$$
$$(N = 74,\ r = 0.989,\ s = 42.42,\ F = 3572.22)$$

These equations may represent the general gas chromatographic behavior of alkylbenzenes and alkylnaphthalenes on the stationary phases and range of temperatures considered. Probably, they could also be used to predict the behavior in other stationary phases.

Concerning polycyclic aromatic hydrocarbons, boiling temperatures are not available in many cases in the literature and also there are not enough I data at different temperatures. For this reason, only the expression $I = f(t_B, p)$ was considered, obtaining the following expression:

$$I = 6.166t_B + 14.498p - 311.297 \qquad (13)$$
$$(N = 50,\ r = 0.990,\ s = 67.49,\ F = 2147.56)$$

CONCLUSIONS

Van der Waals volume may be used as a molecular parameter in gas-chromatography to elucidate the basic skeleton of polycyclic aromatic hydrocarbons.

It is possible to obtain general equations that relate the retention index with boiling point, column temperature and stationary phase polarity, which may be applied to predictions of retention indices and to study the chromatographic behavior of aromatic hydrocarbons.

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