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Note

Comparison of molecular connectivity and a chromatographic correlation factor in reversed-phase high-performance liquid chromatography for polycyclic aromatic hydrocarbons

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Molecular connectivty (χ) has been used to correlate molecular structure with various physical and biological properties[1–7]. Randić[8] developed the concept of molecular connectivity and discussed the relationship of molecular branching to molecular connectivity. Molecular connectivity has been used to predict retention indices of polycyclic aromatic hydrocarbons (PAHs) and other compounds in gas chromatography[9–11]. Karger *et al.*[12] employed molecular connectivity for estimating non-polar group contributions to retention in reversed-phase liquid chromatography.

To determine the usefulness of molecular connectivity for PAHs and hydroaromatics on a reversed-phase high-performance liquid chromatographic (HPLC) column, the retention of thirty-four compounds was measured on a μBondapak C_{18} column with a methanol–water mobile phase. Alkyl-substituted and hydroaromatic compounds were included. Log capacity factor (k') was plotted as a function of χ and compared with graphs of log k' as a function of F (F is a chromatographic correlation factor developed by Schabron *et al.*[13] which relates compound structure to k' on a μBondapak C_{18} column).

EXPERIMENTAL

Instrumentation

The liquid chromatograph used was a Waters model ALC/GPC 244 equipped with a Model 6000A pump, a U6K injector, a Model 440 absorbance detector set at 254 nm and 280 nm, and a strip chart recorder. A 10-μm particle size μBondapak C_{18} column (30 cm × 3.9 mm I.D.) from Waters was used with methanol–water (65:35) at 1.0 ml/min and ambient temperature.

Reagents

Baker HPLC-grade methanol was filtered through a Millipore type F-H 0.45-μm filter. Distilled water was filtered through a Millipore type G-S 0.22-μm filter. Cyclohexane (99 + % from Aldrich, Milwaukee, WI, U.S.A.) or pure-grade *n*-hexane

(99% minimum from Phillips, Borger, TX, U.S.A.) were used to dissolve standard compounds. 1.2-Dihydropyrene was obtained from Laramie Energy Technology Center and 1,2,6,7-tetrahydropyrene was obtained from Pittsburgh Energy Technology Center. All other compounds were obtained from commercial sources and purified when necessary.

Cyclohexane or n-hexane standard solutions were injected into the HPLC system. Amounts injected were 1–12 μg depending on the compound. Each solution was injected at least twice. The void volume of the μBondapak C_{18} column was determined to be 2.75 ml by eluting methanol.

Calculations

Molecular connectivity was calculated with the equation below.

$$\chi = \Sigma \, (\delta_i \cdot \delta_j)^{-1/2}$$

The values of δ can be 1, 2, 3, or 4 corresponding to the number of bonds associated with atoms i and j. The hydrogen atom bonds are neglected. An example calculation is shown below for 2,3-dimethylnaphthalene.
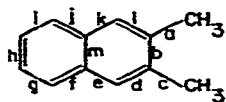
$$\chi = \frac{1}{(1 \cdot 4)^{1/2}} + \frac{1}{(4 \cdot 4)^{1.2}} + \frac{1}{(1 \cdot 4)^{1/2}} + \frac{1}{(4 \cdot 3)^{1/2}} + \frac{1}{(3 \cdot 4)^{1/2}} +$$
$$\quad\;\; (a) \qquad\quad (b) \qquad\quad (c) \qquad\quad (d) \qquad\quad (e)$$

$$\frac{1}{(4 \cdot 3)^{1/2}} + \frac{1}{(3 \cdot 3)^{1/2}} + \frac{1}{(3 \cdot 3)^{1/2}} + \frac{1}{(3 \cdot 3)^{1/2}} + \frac{1}{(3 \cdot 4)^{1/2}} +$$
$$\quad\;\; (f) \qquad\quad (g) \qquad\quad (h) \qquad\quad (i) \qquad\quad (j)$$

$$\frac{1}{(4 \cdot 3)^{1/2}} + \frac{1}{(3 \cdot 4)^{1/2}} + \frac{1}{(4 \cdot 4)^{1/2}} = 4.23$$
$$\quad\;\; (k) \qquad\quad (l) \qquad\quad (m)$$

The chromatographic correlation factor, F, was calculated using the equation below[13].

F = number of double bonds + the number of primary and secondary carbons − 0.5 for a non-aromatic ring

An example calculation for 9,10-dihydroanthracene is

$$F = 6 + 2 - 0.5 = 7.5$$

RESULTS AND DISCUSSION

A comparison of log k', χ, and F values is given in Table I for the thirty-four compounds investigated. Fig. 1 gives a graph of log k' versus χ. Least-squares analysis gave an intercept of -0.55, a slope of 0.30, and a correlation coefficient of 0.97. Fig. 2 shows a graph of log k' versus F. Least-squares analysis gave an intercept of -0.58, a slope of 0.21, and a correlation coefficient of 0.99.
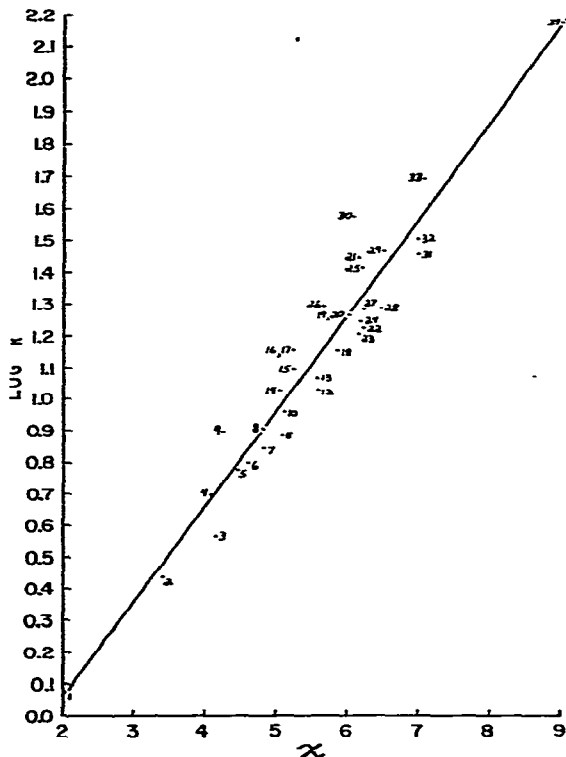

Fig. 1. Graph of log k' versus molecular connectivity.
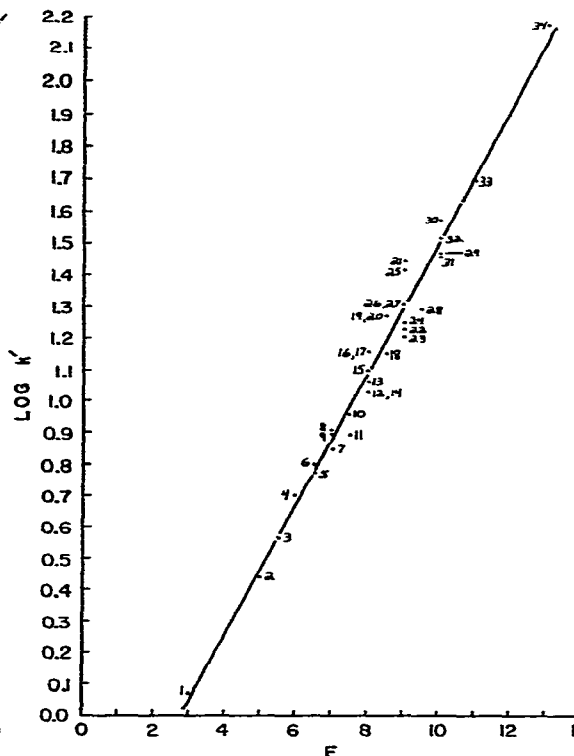
Fig. 2. Graph of log k' versus chromatographic correlation factor.

Comparison of Figs. 1 and 2 shows that less scatter was obtained with F, indicating that a better correlation was achieved with the chromatographic correlation factor than with molecular connectivity, χ. The alkyl-substituted PAHs, hydroaromatics and the parent PAHs all show a good correlation with F. F has also been shown to give good correlation with log k' for other substituted PAHs and hydroaromatics on a similar reversed-phase system[13]. Fig. 1 shows that 1,2,3,4,5,6,7,8-octahydroanthracene (compound 30) lies far from the least-squares line, whereas in Fig. 2 it is very close to the least-squares line. Also, acenaphthylene (compound 3) is far from the least-squares line in Fig. 1 but very close to the least-squares lines in Fig. 2. Several other comparisons like the previous two can be made, indicating F should be more useful in predicting log k' values than χ. The previous conclusion is important because of the variety of chemical structures investigated, namely PAHs, alkyl-substituted PAHs, and hydroaromatics. It seems that the chromatographic corre-

TABLE I

log k', F AND χ VALUES FOR THE COMPOUNDS INVESTIGATED
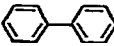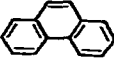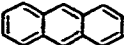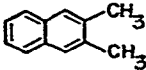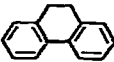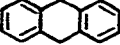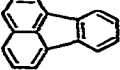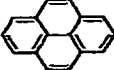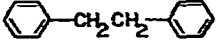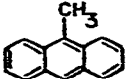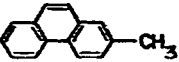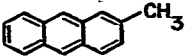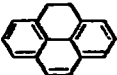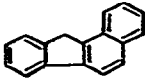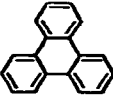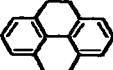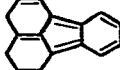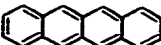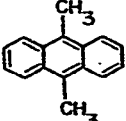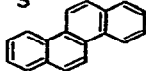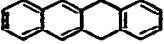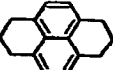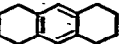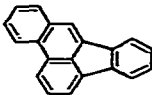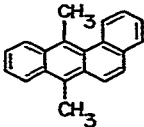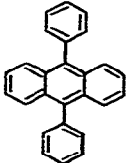
Compound	Structure	log k'	F	χ
1 Benzene		0.073	3.0	2.00
2 Naphthalene		0.44	5.0	3.40
3 Acenaphthylene		0.57	5.5	4.15
4 Biphenyl		0.70	6.0	4.07
5 Acenaphthene		0.78	6.5	4.45
6 Fluorene		0.80	6.5	4.61
7 Phenanthrene		0.85	7.0	4.82
8 Anthracene		0.91	7.0	4.81
9 2,3-Dimethylnaphthalene		0.90	7.0	4.23
10 9,10-Dihydrophenanthrene		0.96	7.5	5.11
11 9,10-Dihydroanthracene		0.89	7.5	5.07
12 Fluoranthene		1.03	8.0	5.56
13 Pyrene		1.07	8.0	5.56
14 Bibenzyl		1.03	8.0	5.03
15 9-Methylanthracene		1.10	8.0	5.23
16 2-Methylphenanthrene		1.16	8.0	5.23

TABLE I *(continued)*

Compound	Structure	*log k'*	*F*	*χ*
17 2-Methylanthracene		1.16	8.0	5.22
18 1,2-Dihydropyrene		1.16	8.5	5.86
19 1,2-Benzofluorene		1.27	8.5	6.02
20 2,3-Benzofluorene		1.27	8.5	6.02
21 *p*-Terphenyl		1.45	9.0	6.14
22 Triphenylene		1.23	9.0	6.23
23 1,2,6,7-Tetrahydropyrene		1.21	9.0	6.15
24 1,2,3,4-Tetrahydrofluoranthene		1.25	9.0	6.17
25 Tetracene		1.42	9.0	6.21
26 9,10-Dimethylanthracene		1.30	9.0	5.66
27 Chrysene		1.29	9.0	6.23
28 5,12-Dihydrotetracene		1.29	9.5	6.47
29 1,2,3,6,7,8-Hexahydropyrene		1.47	10.0	6.49
30 1,2,3,4,5,6,7,8-Octahydroanthracene		1.58	10.0	6.07
31 Perylene		1.46	10.0	6.98

TABLE I *(continued)*

Compound	Structure	log k'	F	χ
32 3,4-Benzofluoranthene		1.51	10.0	6.98
33 7,12-Dimethylbenz[a]anthracene		1.70	11.0	7.06
34 9,10-Diphenylanthracene		2.18	13.0	8.98

lation factor, F, should have considerable applicability in reversed-phase chromatography work with PAHs, alkyl-substituted PAHs, and hydroaromatics. For example, F could be used to predict k' values for several compounds using graphs similar to the one in Fig. 2. Also, if the k' value of an unknown compound is known, then F for the compound can be determined and used to predict various structural features of the compound. Schabron *et al.*[13] have already presented several examples of these approaches.

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