Note

Prediction of retention indices of aromatic hydrocarbons on phases of different polarity

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Since our previous paper[1] concerning the calculation of retention indices of isoparaffins on different phases and at different temperatures, several reports have been appeared on this topic. Tejedor[2] suggested a method for phases with polarities not higher than those of Ucon 50 HB 280X, but applicable only at temperatures close to 373°K. Gassiot-Matas and Firpo-Pamies[3] reported a very interesting method based on molecular connectivity and electrostatic interaction. No data are available to permit an assessment of this method in the case of aromatic hydrocarbons. Our attempt to use molecular connectivity and dipole moment for predicting the retention of aromatic hydrocarbons was unsuccessful.

In the present work a better prediction of retention index is obtained, based on the same concept as in the case of the isoparaffins[1]. The relative retention is assumed to be a function of the vapour pressure, the molecular volume and some characteristic structural elements of the solute. The numerical value thus obtained is named the theoretical retention index, I^{theor}. The results of this work are discussed with respect to the comprehensive studies of Soják and co-workers[4–6] on the retention of aromatic hydrocarbons.

THEORETICAL

The calculation is based on the precise values of indices for aromatic hydrocarbons given in the literature: squalane and 1,2,3-tris (2-cyanoethoxypropane (TCEP)[+], SE-30 and Citroflex A-4[7], Ucon LB 550X and Carbowax 20M[8] and polyethylene glycol-400 (PEG-400)[9].

A study of the literature data shows that the more polar the phase the greater is the dispersion of the experimental results. For example, the greatest difference is 5 i.u. on squalane (for 1,2,3,4-tetramethylbenzene[4,10]), 8.5 i.u. on Citroflex A-4 (for 1,2,4-trimethylbenzene[4,10]), 19 i.u. on PEG-400 (for pentamethylbenzene[8,10]) and 76 i.u. on Carbowax 20M (for hexamethylbenzene[8,10]). However, the mean difference is generally about 3 i.u. Thus, we have excluded from our investigation the substances having the greatest discrepancies between their experimental index values, and have restricted the matrix to mono- and disubstituted aromatic hydrocarbons.

The value of the theoretical retention index is obtained according to

$$I^{theor} = PCI + StN \tag{1}$$

where the physico-chemical index, PCI, and structural number, StN, are expressed as:

$$PCI = 100n + 100 \cdot \frac{\log (p_n^0 V_n / p_i^0 V_i)}{\log (p_n^0 V_n / p_{n+1}^0 V_{n+1}} \tag{2}$$

$$StN = A + B[n_0 + n_R + n_t + 2n_q + r - (n_{CH_3}/n_b)] + C[(n_R/n_0) + n_v - n_t^{o,m}] \tag{3}$$

TABLE I

COMPARISON BETWEEN EXPERIMENTAL AND THEORETICAL INDICES OF AROMATIC HYDRO-CARBONS ON PHASES OF DIFFERENT POLARITY

Hydrocarbon	Squalane[4]		SE-30[7]		Ucon LB 550X[8]	
	I_{80}^{exp}	I_{80}^{theor}	I_{65}^{exp}	I_{65}^{theor}	I_{100}^{exp}	I_{100}^{theor}
Benzene	644.4	644.5	654.8	650.6	759.7	763.0
Toluene	751.7	748.6	757.6	754.3	863.4	863.4
Ethylbenzene	841.6	840.2	849.1	846.8	951.5	953.6
n-Propylbenzene	929.7	928.9	938.1	940.9	1039.3	1041.6
n-Butylbenzene	1029.4	1030.2	1037.4	1042.3	1137.1	1138.5
n-Pentylbenzene	1128.6	1130.9	1135.2	1134.0	1235.4	1238.4
Isopropylbenzene	901.0	901.1	910.1	906.6	1008.3	1006.1
Isobutylbenzene	982.3	981.7	993.1	986.5	1083.2	1080.7
sec.-Butylbenzene	983.1	982.7	993.1	987.1	1088.8	1085.0
tert.-Butylbenzene	967.1	968.1	975.4	972.9	1075.0	1073.6
p-Xylene	855.7	852.4	857.8	857.8	962.9	954.9
m-Xylene	857.8	858.4	857.8	862.9	966.6	966.2
o-Xylene	877.3	875.8	878.9	883.9	999.6	995.1
1-Methyl-4-isopropylbenzene	1004.4	1000.5	1003.2	1005.5	1099.7	1105.7
1-Methyl-3-isopropylbenzene	997.4	992.1	998.2	997.8	1095.3	1098.6
1-Methyl-2-isopropylbenzene	1010.4	1005.2	1016.9	1010.4	1114.5	1113.0
1-Methyl-4-n-propylbenzene	1033.0	1031.4	1035.4	1036.4	1130.3	1131.8
1-Methyl-3-n-propylbenzene	1027.8	1028.2	1031.6	1033.5	1126.3	1128.0
1-Methyl-2-n-propylbenzene	1039.4	1040.1	1045.8	1045.1	1144.5	1146.6
1-Methyl-4-ethylbenzene	945.3	946.0	948.2	950.1	1050.1	1050.8
1-Methyl-3-ethylbenzene	943.1	944.6	948.2	949.6	1050.1	1049.9
1-Methyl-2-ethylbenzene	958.3	960.6	963.2	965.6	1071.6	1073.1
1,4-Diethylbenzene	1033.8	1036.5	–	–	1135.9	1139.2
1,3-Diethylbenzene	1023.2	1027.8	1031.5	1033.4	1127.2	1129.4
1,2-Diethylbenzene	1032.9	1036.0	1042.9	1041.1	1142.3	1143.3

Here p_n^0, $p_{n\pm1}^0$, p_i^0 are the vapour pressures of n-paraffins with n and $n+1$ carbon atoms and of the investigated ith benzene homologue at the analysis temperature, V_n, V_{n+1}, V_i are the corresponding molecular volumes, n_0 is the total number of carbon atoms in the benzene homologue, n_R is the number of substituents R in the benzene homologue, n_t is the number of tertiary carbon atoms in R, n_q is the number of quaternary carbon atoms in R, r is the distance (in number of carbon atoms) between the aromatic ring and the branched carbon atoms in R, n_{CH_3} is the number of methyl groups, n_b is the number of carbon atoms in the substituents of the benzene homologue, n_v is the number of vacant positions in the ring, bearing in mind the symmetry of the molecule, $n_t^{o,m}$ is the number of tertiary carbon atoms at the *ortho* and *meta* positions and A, B, C are constants.

Citroflex A-4[7]		Carbowax 20 m[8]		PEG-400[9]		TCEP[+]	
I_{70}^{exp}	I_{70}^{theor}	I_{100}^{exp}	I_{100}^{theor}	I_{82}^{exp}	I_{82}^{theor}	I_{80}^{exp}	I_{80}^{theor}
779.9	777.4	939.3	941.1	985	987.1	1128.2	1139.0
881.1	879.7	1033.2	1036.1	1079	1070.9	1219.1	1220.1
971.2	968.8	1117.6	1119.2	1160	1159.9	1289.8	1291.8
1056.4	1055.6	1197.0	1198.6	1236	1237.7	1349.9	1361.4
1157.3	1155.3	1291.2	1292.6	1331	1330.2	1431.3	1445.8
1260.7	1259.9	—	—	—	—	1506.4	1527.9
1029.4	1027.0	1160.9	1164.7	1202	1203.4	1319.5	1322.5
1105.3	1103.7	1220.1	1228.0	1262	1264.7	1363.1	1367.8
1108.4	1106.1	1235.0	1238.6	1270	1274.6	1371.7	1385.5
1095.7	1090.7	1222.9	1217.0	1262	1253.3	1372.7	1358.5
978.5	976.6	1124.9	1125.4	1167	1165.0	1302.1	1291.3
981.4	985.4	1131.5	1130.6	1172	1169.7	1306.1	1296.2
1007.9	1012.5	1172.5	1172.8	1217	1214.1	1357.5	1354.0
1123.7	1123.4	1254.4	1256.1	1290	1291.2	1403.2	1402.6
1119.0	1117.0	1251.1	1252.5	1289	1287.2	1396.4	1400.5
1140.4	1145.1	1282.6	1280.5	1320	1320.6	1439.4	1442.3
1054.7	1056.9	1287.7	1288.0	1323	1324.0	1430.3	1433.2
1051.8	1054.5	1284.5	1284.0	1320	1320.4	1425.0	1429.9
1066.2	1067.7	1313.4	1316.7	1353	1354.9	1467.5	1478.7
1068.8	1070.8	1207.4	1209.2	1249	1247.0	1371.1	1364.6
1068.8	1070.7	1210.0	1208.3	1249	1246.4	1370.4	1364.2
1089.8	1092.2	1243.2	1241.2	1285	1285.0	1415.4	1417.1
1158.0	1160.5	1291.6	1292.6	1328	1329.0	1439.4	1438.3
1149.4	1152.0	1282.8	1283.8	1319	1319.5	1428.4	1429.4
1165.8	1165.8	1306.5	1311.9	1349	1350.4	1465.4	1474.5

A more detailed explanation of the theoretical basis of eqn. 2 is given in ref. 11. Examples of the determination of different structural elements are given in ref. 12.

DISCUSSION

Different values of PCI are obtained at different temperatures of analysis, while the values of StN depend on the structures of both the phase and solute, and on the polarity of the phase. The data given in Table I allow one to compare the calculated and experimental retention indices for 25 C_6–C_{10} aromatic hydrocarbons. The larger error observed for the more polar phases is due probably to poorer reproducibility of the experimental I values.

Nevertheless, the accuracy of the predicted I^{theor} is comparable or better compared with those of the other methods of calculation. Our model has some additional advantages:

(i) the PCI term is temperature dependent;

(ii) the StN term includes the influence of the stationary phase polarity.

If we calculate PCI values of 25 aromatic hydrocarbons at two temperatures, e.g., 100 and 110°C, the mean value of dI/dT is 0.335, which is quite close to the mean experimentally determined value of 0.269. Therefore, the PCI term of I^{theor} takes good account of the changes of I^{exp} with the analysis temperature.

Table II compares I^{theor} at 70°C calculated according to our model with indices obtained experimentally[4] for several compounds at the same temperature. In all cases but two, the differences are statistically insignificant. The greatest difference is 6 i.u. which is comparable with the mean deviation between the experimental I for such compounds obtained on squalane in different laboratories.

TABLE II

COMPARISON BETWEEN EXPERIMENTAL[4] AND CALCULATED RETENTION INDICES FOR AROMATIC HYDROCARBONS ON SQUALANE AT 70°C

F = Fischer criterion.

Hydrocarbon	I^{exp}	$I^{exp}_{avr.}$	I^{theor}	F_{calc}	$F^{0.001}_{table}$
Benzene	642.6; 641.9; 642.0; 642.1; 642.9; 643.4; 645.3	642.7	642.5	0.35	3.92
Toluene	748.9; 749.2; 749.3; 750.2; 750.2; 750.4; 750.8; 751.2; 751.9	750.2	747.5	4.28	7.31
Ethylbenzene	838.7; 838.9; 839.8; 839.8; 840.0; 840.1; 840.7; 842.0	839.9	838.3	1.94	7.31
p-Xylene	853.0; 853.2; 854.0; 854.1; 854.2; 854.4; 854.5; 856.2; 856.2	854.4	848.0	16.14	7.31
m-Xylene	854.1; 855.3; 855.9; 856.0; 856.6; 856.7; 858.3	856.1	851.2	5.6	3.92
o-Xylene	874.1; 874.4; 875.1; 875.3; 875.3; 875.5; 875.5; 876.0; 877.8	875.4	874.0	1.38	7.31

The values of the constants A, B and C which reflect the complicated relations between the phase and the solute are summarized in Table III. The value of the phase characteristic A' is obtained according to:

$$A' = A_{\text{phase}} - A_{\text{squalane}} \tag{4}$$

It can be compared with the McReynolds benzene polarity[13] of the phases used. The values in the last two columns of Table III, obtained in quite different ways, are almost equal, especially for the non-polar and medium polar phases. The deviations which occur for highly polar phases could be due to the presence of constants B and C in our model[1], which take account of the steric influence of the stationary phase.

TABLE III

VALUES OF COEFFICIENTS A, B AND C OF StN FOR AROMATIC HYDROCARBONS SEPARATED ON PHASES OF DIFFERENT POLARITY

Stationary phase	A	B	C	A'	McReynolds benzene polarity
Squalane	−47	3.48	−0.77	0	0
SE-30	−37	3.47	−0.74	10	15
Ucon LB 550X	67	0.22	0.80	114	118
Citroflex A-4	88	1.92	0.73	135	135
Carbowax 20M	245	−4.18	4.24	292	325
PEG-400	295	−5.65	4.84	342	345
TCEP	448	−12.92	8.48	495	593

In conclusion, the model proposed allows one to calculate the values of I^{theor} for a given mixture of aromatic hydrocarbons on a phase chosen "*a priori*" and to decide whether an analysis would be justified. If the separation is not satisfactory and a change of temperature seems desirable, only the PCI term need be recalculated. If the phase is to be changed, only the StN term must be recalculated.

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