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QUANTITATIVE RELATIONSHIPS BETWEEN THE STRUCTURE OF ALKYLBENZENES AND THEIR GAS CHROMATOGRAPHIC RETENTION ON STATIONARY PHASES WITH DIFFERENT POLARITY

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SUMMARY

The retention indices of 28 C_6–C_{10} and n-C_{11} alkylbenzenes were determined on silicone oil OV-101, UCON LB-550-X, Carbowax 20M and TCEP. Additionally, retention indices of the same compounds on squalane, PEG-4000 and Carbowax 1540 were taken from the literature for quantitative structure–retention investigations. A general mode for deriving adequate precalculation equations was used. Two different kinds of regressors were studied.

The best results, presented as the maximum discrepancy between the experimental and calculated retention indices, are 1.5 for squalane, 2.5 for OV-101, 2.9 for UCON, 2.4 for Carbowax 20M, 5.6 for Carbowax 1540, 11.3 for PEG-4000 and 7 for TCEP. A very high correlation between the polarity of the studied phases and some of the regressors has been found.

INTRODUCTION

Recently, an adequate equation for the precalculation of the retention indices of alkylbenzenes on squalane has been proposed[1]. This stationary phase is widely applied in petroleum analysis but, especially for alkylbenzenes, stationary phases such as silicone oil OV-101[2,3] or equivalents, more polar phases such as Carbowax 20M[4,5] and even strongly polar phases such as TCEP (triscyanoethoxypropane)[6] are preferred.

The derivation of equations for the precalculation of the retention indices of alkylbenzenes on phases more polar than squalane is of practical interest. There have been many investigations to find a satisfactory correlation between the retention and physico-chemical properties or topological and/or electronic indices of the alkylbenzenes (*e.g.*, refs. 7–11), but the discrepancies between the calculated values ($I_{calc.}$) and the experimentally obtained retention indices (I) are too great.

A new model has now been used for deriving an adequate equation for the precalculation of the retention indices of alkylbenzene. The model is based on the assumption that the retention is an additive property depending on some basic and

several tuning contributors[12]. The value of $I_{calc.}$ obtained from the basic contributor(s) is 90–110% of the $I_{exp.}$ value. The deviations are then compensated by addition of suitable tuning contributors. As the basic and tuning contributors in this study, all of the indices given previously[1] were considered. The retention indices of 28 C_6–C_{10} and n-C_{11} alkylbenzenes were obtained experimentally on OV-101, UCON LB-550-X, Carbowax 20M and TCEP. Unified retention indices on squalane[13] and literature data for the retention indices of alkylbenzenes on Carbowax 1540[14] and Carbowax 4000[11] were also included.

EXPERIMENTAL

The retention indices of the alkylbenzenes studied were determined on fused-silica capillary columns with flame ionization detection under the following conditions (stationary phase, column dimensions, column temperature, splitting ratio): OV-101, 50 m × 0.25 mm I.D., 100°C, 1:80; UCON LB-550-X, 50 m × 0.32 mm I.D., 100°C, 1:80; Carbowax 20M, 30 m × 0.32 mm I.D., 100°C, 1:100; and TCEP, 30 m × 0.32 mm I.D., 80°C, 1:100.

The retention times of n-alkanes on the column with TCEP showed poor repeatability. To obtain more reliable results, their retention time was calculated from the regression equation of their retention at different temperatures.

DATA HANDLING AND RESULTS

The general model given previously[12] was rearranged to the equation

$$I_{calc.} = b_0 + b_1 I_p + \Sigma b_j T_j$$

where I_p is the vapour pressure index, proposed by Bonastre and Grenier[15], T_j are selected tuning structural indices and b_0, b_1 and b_j are constants (estimates of the parameter contributions).

The indices selected are explained after the corresponding equations. The criteria used for selection are the values of the variance and the maximum discrepancy between $I_{exp.}$ and $I_{calc.}$ ($\Delta_{max.}$). The best equations are presented in Table I.

The upper limit of the number of parameters is taken as eight in order to avoid chance correlations[16]. A decrease in the number of parameters depends on the accuracy required. It is seen from Table I that equations with different numbers of parameters have the same value of $\Delta_{max.}$. Hence several equations might be derived, depending on the availability of values for the tuning indices. These equations might be used not only for the exact precalculation of the retention indices in the interpolation region, but also for predictive calculations. From a statistical point of view, the equations with the least number of independent regressors have the best extrapolation possibilities. These requirements are fulfilled only for eqns. 7, 8, 9 and 19, because the intercorrelation between I_p, X_1, E_{LUMO}, qA and qB and qT is insignificant. This is why the predictive ability was checked for a large number of equations. Two compounds, namely 1,2,3-trimethylbenzene (123TMB) and n-pentylbenzene (nPeB) were removed from the initial set of retention data. 123TMB has a unique structure with its three neighbouring substituents and differs substantially from all other alkylarenes with

nine carbon atoms. nPeB is a homologue of n-alkylbenzenes, but with its eleven carbon atom lies in the extrapolation n_C region. New constants for the corresponding predictive equations were calculated:

$$I_{SQ} = 155.9 + 0.97994 \, I_p - 13.34 \, X1 - 26.12 \, E_{LUMO} + 28.48 \, qA \qquad (1)$$

$$I_{OV-101} = 21.3 + 0.9808 \, I_p + 6.172 \, X1 + 118.67 \, qA - 60.42 \, qB + \\ + 1.115 \, qT \qquad (2)$$

$$I_{UCON} = 104.8 + 1.14009 \, I_p - 3.62 \, L_{max} - 0.4536 \, \varepsilon + 98.87 \, qA - \\ - 155.6 \, qB + 35.1 \, qT \qquad (3)$$

$$I_{C-20M} = 148.4 + 1.37267 \, I_p - 6.265 \, L_{max} + 20.59 \, E_{LUMO} - \\ - 1.1868 \, \varepsilon + 233.7 \, qA - 177.79 \, qB \qquad (4)$$

$$I_{TCEP} = 404.4 + 1.60548 \, I_p - 13.5 \, L_{max} - 2.0216 \, \varepsilon + 331.86 \, qA - \\ - 335.48 \, qB + 56.47 \, qT \qquad (5)$$

where

$X1$ is the first eigenvector in the graph spectrum of the solute molecule;

L_{max} is the maximum geometric distance between the atoms of the solute molecule;

ε is l'Haya's electropy index[17];

E_{LUMO} is the energy of the LUMO orbitals of the solute molecule; all quantum chemical calculations were done at VHTI, Burgas, by the standard CNDO method;

qA is the sum of the absolute charges of the carbon atoms in the functional group;

qB accounts for the charges of carbon atoms at α-positions to the aromatic ring; and

qT is the sum of the absolute charges of all carbon atoms in the solute molecule[18].

The value of the predicted retention index, $I_{pred.}$ of n-PeB and 123TMB and also the values of I_{calc} are compared with the experimental values in Table II.

To establish the significance of the parameters in equation 1–5 for the quantitative relationships between the retention and the structure of the alkylbenzenes, the same indices were applied to retention data for alkylbenzenes obtained by other workers on the same or different stationary phases. The new equations obtained (eqns. 6–8) are similar to eqns. 3–5 in the magnitudes of the parametric estimates and have the same sign, accuracy and predictive possibilities.

$$I_{UCON} = 99.7 + 1.15484 \, I_p - 2.93 \, L_{max} - 0.52 \, \varepsilon + 169.1 \, qA - \\ 197.4 \, qB + 56.6 \, qT \qquad (6)$$

TABLE I

PARAMETRIC ESTIMATIONS (b_1–b_j) OF THE REGRESSORS USED AND VALUES OF THE MAXIMUM DISCREPANCY (Δ_{max}) BETWEEN $I_{exp.}$ AND $I_{calc.}$

Stationary phase	Eqn. No.	No. of regressors	b_1 (I_p)	b_2 ($X1$)	b_3 (E_{LUMO})	b_4 (qA)	b_5 (qB)	b_6 (L_{max})	b_7 (ε)	b_8 (qT)	Δ_{max} (i.u.)
Squalane	1	8	0.99685	−21.68	−24.623	32.07	4.47	−0.55	−0.020	−8.148	1.4
	2	7	0.9987	−22.25	−26.42	40.70	−12.37	−0.60	−0.021		1.5
	3	7	0.99731	−21.61	−25.083	34.52		−0.55	−0.020	−6.23	1.5
	4	7	0.99486	−14.55	−22.783	36.06	5.45		−0.039	−9.05	1.7
	5	6	0.98282	−15.29	−25.68	26.85	11.56			−11.91	1.7
	6	6	0.9954	−14.4	−23.33	39.10				−6.72	1.7
	7	5	0.98326	−15.01	−27.06	32.97			−0.040	−6.94	1.7
	8	5	0.98358	−15.03	−28.53	39.28	−13.06				1.7
	9	4	0.98235	−16.71	−26.66	30.22					1.8
	10	3	0.97619		−23.08	25.52					2.5
OV-101	11	8	0.96272	−1.88	−2.00	89.89	−36.84	−0.89	0.069	−8.13	2.7
	12	7	0.95895	−2.39	1.79	69.71		−0.85	0.076	−23.90	2.5
	13	7	0.96447	−2.11	−3.72	98.65	−53.70	−0.93	0.067		2.5
	14	7	0.97377	7.98	3.60	105.36	−42.60	−0.19		−6.05	2.5
	15	6	0.97094	10.35	3.73	105.13	−41.16			−6.87	2.5

No.	Phase	n									
16		5	0.97245	9.12		115.07	− 59.48	− 0.22		0.73	2.5
17		5	0.97566	6.23		113.86	− 58	− 0.74		− 24.54	2.5
18		5	0.954			68.13			0.086		2.5
19		4	0.9725	8.98		114.5	− 58.21	− 0.49			2.5
20		4	0.98036			112.76	− 56.15				2.5
21	UCON-LB-550X	8	1.12489	− 0.22	− 4.45	144.46	− 189.83	− 3.06	− 0.41	46.31	2.4
22		7	1.11592	− 1.78	4.76	93.59	− 93.28	− 2.99	− 0.40		3.0
23		7	1.1248		− 4.41	144.54	− 189.92	− 3.05	− 0.41	46.33	2.9
24		6	1.11513		5.08	94.08	− 93.72	− 2.91	− 0.40		3.0
25		6	1.14247			104.8	− 162.37	− 3.39	− 0.46	37.54	2.8
26		5	1.10758			92.49	− 98.34	− 2.93	− 0.37		3.6
27	Carbowax 20M	8	1.4189	− 24.6	4.24	243.75	− 281.94	− 8.1	− 1.23	0.05	4.7
28		7	1.3853	− 22.25	17.4	230.48	− 175.91	− 7.3	− 1.17		6.3
29		7	1.4179	− 28.88		241.85	− 289.49	− 8.37	− 1.21	58.78	4.8
30		6	1.4064			254.37	− 309.36	− 7.03	− 1.246	64	6.3
31		6	1.3802		22.39	240.4	− 179.84	− 6.16	− 1.21		5.8
32		5	1.3469			233.4	− 200.21	− 6.24	− 1.09		6.1
33	TCEP	8	1.5998	0.035	4.11	347.36	− 346.9	− 12.07	− 2.087	0.06	6.8
34		7	1.5663	0.038	17.64	333.97	− 239.41	− 11.22	− 2.024		7
35		7	1.6085		− 3.94	331.72	− 341.99	− 13.84	− 2.018	0.06	7.2
36		6	1.6100			331.78	− 332.27	− 13.78	− 2.03	53.72	7
37		5	1.5613			314.22	− 241.12	− 13.12	− 1.9		8.0

TABLE II

COMPARISON OF $I_{calc.}$ OF 26 C_6–C_{10} ALKYLBENZENES AND $I_{pred.}$ OF n-PeB AND 123TMB WITH $I_{exp.}$ ON SIX STATIONARY PHASES WITH DIFFERENT POLARITY

No.	Alkylbenzene	Squalane		OV-101		UCON LB		Carbowax 20M		TCEP	
		$I_{exp.}$	$I_{calc.}$	$I_{exp.}$	$I_{calc.}$	$I_{exp.}$	$I_{calc.}$	$I_{exp.}$	$I_{calc.}$	$I_{exp.}$	$I_{calc.}$
1	Benzene (B)	650.4	649.6	663	660.7	760	760.9	935	931.2	1127	1122.4
2	Toluene (MB)	757.6	757.7	766	765	864	863	1032	1030.6	1219	1217.0
3	EthylB (EtB)	847.5	847.3	857	856	952	954.5	1117	1119.3	1289	1290.2
4	n-PropylB (nPrB)	936.3	936.4	947.5	947.4	1038.5	1037.6	1197	1198.1	1350	1351.4
5	n-ButylB	1036.2	1037.0	1046	1048.6	1136	1134.9	1291	1290.6	1431	1429
6	iPrB	907.5	909.2	919	920.4	1009	1010.4	1164	1167.7	1320	1324.1
7	iBuB	989.9	990.0	1002	1002.6	1083	1083.1	1228	1233.8	1365	1372.2
8	sec.-BuB	990.0	991.4	1004	1003.1	1089	1088.5	1235	1237.3	1372	1378.9
9	tert.-BuB	973.3	973.7	986	988	1075	1072.1	1223	1224.4	1373	1373.1
10	p-Xylene	861.9	862.6	866	865.5	963	961.3	1126	1127.6	1304	1307.9
11	m-Xylene	864.4	863.9	866	866.4	966	964.8	1130	1130	1308	1308.5
12	o-Xylene	884.0	883.6	888	889.4	995	995	1171	1171.5	1359	1360.9
13	1-M-4-iPrB	1010.5	1010.1	1016.5	1017.5	1100	1101.7	1254.5	1254.7	1402	1402.4
14	1-M-3-iPrB	1002.8	1002.0	1010	1008.6	1094	1093.8	1248	1242.6	1395	1389.1
15	1-M-2-iPrB	1016.9	1015.8	1031	1028.9	1114	1115	1280	1277	1439	1432.8
16	1-M-4-nPrB	1039.8	1039.3	1046.5	1047.4	1131	1131.3	1287.5	1288	1429	1432.3
17	1-M-3-nPrB	1034	1034.6	1042	1041.2	1126	1127.1	1284	1280.2	1425	1424.5
18	1-M-2-nPrB	1046.1	1046.1	1057.5	1055.9	1146	1145.9	1313	1309.1	1467	1462.1
19	1-M-4-EtB	951.5	951.7	957	957.7	1049	1049.3	1208.5	1210.8	1371	1370.6
20	1-M-3-EtB	948.7	949.4	955	953.8	1049	1048.7	1209	1207.4	1371	1369.3
21	1-M-2-EtB	965.3	964.2	973	971.9	1071	1070.6	1242.5	1239.8	1414	1410.5
22	1,4-DiEtB	1040.7	1039.4	1047	1048.6	1136	1136.9	1291.5	1293.7	1439	1438.2
23	1,3-DiEtB	1028.8	1029.3	1038.5	1036.5	1127	1126.3	1282	1277	1427	1420
24	1,2-DiEtB	1039.3	1037.5	1051	1049.3	1144	1144.7	1308.5	1308.9	1465	1465.3
25	1,3,5-TriMB	967.7	968.8	969	970.2	1064	1065	1228	1232.9	1398	1401
26	1,2,4-TriMB	986.3	986.7	988	988.9	1088	1087.1	1260	1261.7	1436	1441
27	n-PentylB	1135.5	1133.9	1144.9	1146.5	1228	1223.8	1381	1379.3	1505	1507.9
28	1,2,3-TriMB	1012.4	1011	1016	1017.6	1121	1121.5	1308	1307.1	1493	1495.4

$$I_{C-1540} = 122.6 + 1.4605\ I_p - 7.67\ L_{max} + 27.58\ E_{LUMO} - 1.3815\ \varepsilon +$$
$$+ 271\ qA - 190.3\ qB \qquad (7)$$

$$I_{TCEP} = 352.8 + 1.5484\ I_p + 33.9\ X1 - 10.92\ L_{max} - 1.9284\ \varepsilon +$$
$$+ 352.8\ qA - 300.8\ qB \qquad (8)$$

The values of $I_{calc.}$ calculated according to eqns. 6–8 are compared with the literature values of $I_{exp.}$ in Table III. Coincidence of the $I_{calc.}$ and $I_{exp.}$ values is evident even for the data on PEG-4000, which are greater than those on TCEP and seemed to be unreliable.

Obviously, any data obtained on a particular column might be used to calculate the parametric estimates valid for this column. Once available, the equation might be used for predictive calculations, to search for the best analysis temperature (the

TABLE III

COMPARISON OF $I_{calc.}$ WITH $I_{exp.}$ OF DIFFERENT ALKYLBENZENES OBTAINED ON UCON-LB-550-X BY DÖRING *ET AL.*[4], ON CARBOWAX 1540 BY KUMAR *ET AL.*[14], ON PEG-4000 BY HÉBERGER[11] AND ON TCEP BY SOJÁK AND RIJKS[6]

No.	Alkylbenzene	UCON LB		Carbowax 1540		PEG-4000		TCEP	
		$I_{calc.}$	$I_{exp.}$	$I_{calc.}$	$I_{exp.}$	$I_{calc.}$	$I_{exp.}$	$I_{calc.}$	$I_{exp.}$
1	Benzene (B)	759.7	760.5	965.3	958.8	1270	1266	1128.2	1122.7
2	Toluene (MB)	864.3	863	1060.8	1060	1549	1548.1	1219.1	1216.2
3	EthylB (EtB)	951.5	954.5	1145.2	1150.2	1802	1802.8	1289.8	1290.4
4	*n*-PropylB	1039.3	1039.2	1227.3	1229.5	2050	2051.5	1349.9	1352.5
5	*n*-ButylB	1135.1	1136.2	1325	1323			1431.3	1431.2
6	*n*-PentylB	1233.4	1229.5	–	–			1506.4	1505.5
7	iPrB	1008.3	1010.9	1193.3	1198.2			1319.5	1325.4
8	iBuB	1083.2	1084.2	1258.2	1264.2			1363.1	1372.8
9	*sec.*-BuB	1088.8	1087.8	1266.7	1267.5			1371.7	1379.6
10	*tert.*-BuB	1075	1073.2	1254	1255.5			1372.7	1372.7
11	*p*-Xylene	962.9	961.7	1154	1158.4	1830	1832.8	1302.1	1307
12	*m*-Xylene	966.6	965.4	1161.1	1161.6	1844	1832.7	1306.1	1305.9
13	*o*-Xylene	999.6	994.3	1204.5	1206.5	1975	1977.8	1357.5	1360.7
14	1-M-4-iPrB	1099.7	1101.8	1284.4	1285.6			1403.2	1402.3
15	1-M-3-iPrB	1095.3	1094.3	1281.1	1273.5			1396.4	1386.9
16	1-M-2-iPrB	1114.5	1114.9	1315.5	1312.4			1439.4	1431.8
17	1-M-4-nPrB	1130.5	1132.4	1318.9	1319.9			1430.3	1433.4
18	1-M-3-nPrB	1128.2	1128.7	1315.5	1312.4			1425	1423.5
19	1-M-2-nPrB	1145.9	1146.5	1346.6	1343.6			1467.5	1463.5
20	1-M-4-EtB	1050.1	1049.2	1242	1242.1	2080	2075.5	1372.1	1371
21	1-M-3-EtB	1050.1	1048.9	1243.9	1239.4	2072	2080.6	1370.4	1367.5
22	1-M-2-EtB	1071.6	1073.9	1278.6	1274.2	2193	2188.2	1415	1411.3
23	1,4-DiEtB	1135.9	1136.2	1322.8	1326			1439.4	1439.6
24	1,3-DiEtB	1127.2	1125.9	1313.8	1308.7			1428.4	1419.1
25	1,2-DiEtB	1142.3	1142.7	1342	1344.4			1465.4	1466.5
26	1,3,5-TriMB	1066.5	1067.9	1261.6	1268			1387.9	1396.1
27	1,2,4-TriMB	1089.6	1090	1297.5	1297.7			1435.5	1439.9
28	1,2,3-TriMB	1123.6	1125.2	1348.8	1347.1			1493.1	1491

regressor I_p is temperature dependent), to identify or to predict the retentions of additional compounds of the same type, without additional analysis of standard compounds, etc.

If we reconsider the data in Table I, some interesting peculiarities can be observed: (i) the less polar the stationary phase, the greater is the number of equations with equal accuracy (Δ_{max}); (ii) the less polar the stationary phase, the lower is the number of necessary tuning indices for the same Δ_{max}; and (iii) some of the indices increased in importance with increasing polarity of the stationary phase, while others became insignificant.

To evaluate the real significance of the regressors used, the parametric estimates of eqns. 2, 13. 22, 29 and 34 in Table I (equal number of the same parameters) were made equal to the mean value of I_p (taken as 1). The reduced parametric estimations are given in Table IV.

It is seen that I_p is the most significant contributor to the $I_{exp.}$ value and in all instances it is higher by at least one order of magnitude. The index qA is also an important contributor and occurs in all parameter combinations (see Table I). The indices qB and qT might be used interchangeably on stationary phases with low polarity. On polar stationary phases the simultaneous presence of qA, qB and L_{max} becomes necessary. It is interesting that the parametric estimates of L_{max}, E_{LUMO} and ε change almost linearly with the polarity of the stationary phase with respect to benzene, according to McReynolds[19]. For example, (polarity)$_{st.ph.}$ = $-$ 39.47 $-$ 53.6273 b_6, with correlation coefficient 0.996; and (polarity)$_{st.ph.}$ = 10.08 $-$ 282.92 b_7, with correlation coefficient 0.982.

The negative sign of the regression with L_{max} is assumed to be due to the thicker packing of the stationary phase molecules[20,21]. The stronger the intermolecular forces between the stationary phase molecules, the more difficult is the penetration of longer solute molecules. The correlation with ε also has a negative sign. We assume that the greater the space of electron distribution, the weaker are the actions between the solute and stationary phase molecules.

The approach given above gives stable results when applied to data obtained on stationary phases with different polarity and also to data obtained by different workers. It might be used for a preliminary orientation with regard to a suitable stationary phase, for the precalculation of a suitable analysis temperature, for identification without the additional analysis of standard compounds, for the prediction of the retention of new alkylbenzenes, not routinely present in the samples, and for studying retention as a function of the structure of alkylbenzenes.

TABLE IV

REDUCED PARAMETRIC ESTIMATES FOR THE INDICES IN EQNS. 1–5

Stationary phase	I_p	XI	E_{LUMO}	qA	qB	L_{max}	ε
Squalane	0.9987	−0.049	−0.106	0.0041	−0.0012	−0.004	−0.0042
OV-101	0.96447	−0.005	−0.015	0.0099	−0.0054	−0.006	0.0134
UCON LB	1.11592	−0.004	0.019	0.0093	−0.0093	−0.020	−0.0080
Carbowax 20M	1.3853	−0.390	0.069	0.0230	−0.0023	−0.049	−0.2320
TCEP	1.5663	0.079	0.068	0.0333	−0.0239	−0.075	−0.3820

TABLE V

REDUCED PARAMETRIC ESTIMATES(b_1-b_6) OF THE STRUCTURAL FRAGMENTS USED AND THE VALUES OF THE MAXIMUM DISCREPANCY (Δ_{max}) BETWEEN $I_{exp.}$ AND $I_{calc.}$

Stationary phase	b1 (I_p)	b2 (n_0)	b3 (HO)	b4 (H1)	b5 (n_{CH_3}/n_L)	b6 (n_i)	b_0	Δmax (i.u.)
Squalane	1.06718	−0.08	−0.003	−0.0005	0.0028	0.0014	19.4	3.6
OV-101	0.86095	0.1071	0.002	0.0053	−0.0038	−0.0003	49.5	4.7
UCON-LB	0.9379	−0.0012	0.003	0.0077	0.0011	−0.0033	163.5	4.2
Carbowax 20M	1.02265	−0.116	−0.0045	0.0179	0.0036	−0.0061	353.5	3.1
Carbowax 1540	1.08141	−0.1603	−0.009	0.021	0.005	−0.0053	372.9	4.2
TCEP	1.09585	−0.303	−0.009	0.0027	0.0187	−0.0101	610.3	5.9

If no data on the structural indices (topological, geometric and electronic) are available and there is no corresponding software, the structural fragments[22] might alternatively be used as tuning regressors. We selected for study the same structural fragments as given previously[1], to which were added the following: n_i = the number of C–C bonds between the aromatic ring and the branched C atom in the substituent (e.g., in iPrB n_i = 1, in iBuB n_i = 2); n_{CH_3} = the number of CH_3 groups in the compound; and n_L = the number of C–C bonds in the straight chain of the substituent. The results are presented in Table V. With fewer regressors, better results were obtained than previously[23]. Again, for the less polar stationary phases fewer regressors are necessary. Comparison of the variances and the maximum discrepancies shows that they are of the same magnitude, as if structural indices had been used.

The simplicity of the determination of such regressors makes this approach a promising tool for use in routine chromatographic practice.

The data in Table V confirm the stated[20] correlation between the constants b_0 and the polarity (r = 0.9982). In addition, high correlation coefficients exist between the polarity and the parametric estimates of the fragments $H1$ (number of o-substituents) and n_i. A two parametric equation:

$$(\text{polarity})_{st.ph.} = -31.42 + 1.0914\,b_0 - 1723.5\,b_6$$

TABLE VI

COMPARISON OF CALCULATED ($P_{calc.}$) AND EXPERIMENTAL [$P(C_6H_6)$] POLARITIES WITH RESPECT TO BENZENE ACCORDING TO McREYNOLDS

Stationary phase	Polarity	
	$P_{calc.}$	$P(C_6H_6)$[19]
Squalane	−9.6	0
OV-101	13.5	17
UCON LB-550-X	118	133
Carbowax 20M	322	323
Carbowax 1540	371	372
TCEP	593	588

with $r = 0.9993$ describes the stationary phases studied very well, as shown in Table VI. The results obtained on stationary phases with very different polarities, the wide range of alkylbenzenes studied, the different types of tuning parameters used for the derivation of the predictive equations illustrate the potential of the general model for quantitative structure investigations.

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