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RELATIONSHIPS BETWEEN GAS CHROMATOGRAPHIC RETENTION INDICES AND MOLECULAR STRUCTURE OF AROMATIC HYDROCARBONS

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SUMMARY

Regularities of the gas chromatographic behaviour of C_6–C_{13} alkylbenzenes, C_{10}–C_{13} alkylnaphthalenes and C_8–C_{11} alkyl aryl carbamates are described by structural models containing Van der Waals volumes and molecular connectivity indices of different orders. The dependences are shown to be approximated by seven-factor (for alkylbenzenes), five-factor (for alkylnaphthalenes) and three- or five-factor (for alkyl aryl carbamates) polynomials of the first power. The correlation coefficients are 0.998–1.000.

INTRODUCTION

Correlations of chromatographic retention with the physico-chemical and structural characteristics of sample substances form the basis for the choice of appropriate chromatographic systems and are of great significance for solving problems of the identification of components of complex mixtures. Martin[1] was the first to elucidate the quantitative relationships between the structure of dissolved substances and their chromatographic behaviour. He proposed that a substituent changes the distribution coefficient of a dissolved substance by an extent that depends on the nature of the substituent and on the mobile and stationary phases used. This phenomenon is considered to be an example of linear free energy relationships. In this respect the parameters of chromatographic retention that are used in correlation investigations are considered to be proportional to a free energy change that is connected with the process of chromatographic distribution.

With non-polar or low-polarity stationary phases, the retention of compounds on which is determined by dispersion forces, these correlation dependences are based on the assumption of additivity of the free energies of interaction of the sorbates with the stationary phase, which may be calculated by summation of the physico-chemical and structural increments of the molecule.

The additive scheme proposed by Berezkin[2,3] for the calculation of elution characteristics from the structural increments of compounds also assumes additivity of retention indices (I)[4–6], the dependence of which on the molecular characteristics is

described by the equation

$$I = \sum_{i=1}^{n} a_i x_i + b \tag{1}$$

where x_i are physico-chemical and structural parameters of the compounds and a_i and b are constants.

Eqn. 1 is simplified if the linear correlations of I are considered as dependent on one parameter x:

$$I = ax + b \tag{2}$$

Although the field of application of eqn. 2 is limited in most instances to members of the same homologous series, such dependences are worthy of attention and may be used for the preliminary calculation of retention indices of aromatic hydrocarbons[7-12].

The correct choice of molecular characteristics for the construction of a model reflecting the nature of the chemical structure permits the prediction not only of chromatographic behaviour but also general properties of a substance. The molecular connectivity index[13,14] and the Van der Waals volume[15] provide wide opportunities for describing the structure of organic molecules.

According to eqn. 2, a close correlation is established between the retention indices of aromatic hydrocarbons and molecular connectivity indices[16-22] and also between the Van der Waals volume[8-10]. It has been shown that the retention of aromatic hydrocarbons may be described by eqn. 1, which contains connectivity indices of different orders[8,23] and their combinations with the Van der Waals volume[24].

EXPERIMENTAL

The retention indices of the following compounds were used in this study: C_6–C_{13} alkylbenzenes, obtained on open-tubular columns with squalane at $100°C$[25] and OV-101 at $100°C$[26]; C_{10}–C_{13} alkylnaphthalenes, obtained on open-tubular columns with heptaphenyl ether (HPE)[8] and OV-101 at $140°C$[26]; and C_8–C_{11} alkyl aryl carbamates, obtained on a packed column with 5% SE-30 on Chromaton N AW HMDS (0.2–0.25 mm) at $140°C$[27].

In eqn. 1, the Van der Waals volume and connectivity indices of different orders were taken as independent variables. The Van der Waals volumes (V_W) were calculated according to Bondi[15] by summation of the contributions of the volumes of individual groups forming the compound. The path connectivity (χ_p) and cluster ($^3\chi_c$, χ_{pc}) indices of the five orders were calculated according to Kier and Hall[14]. For connectivity indices of the third to fifth orders, the total values of the path and cluster parameters were also determined, $i.e.$, $^3\chi_{p+c}$, $^4\chi_{p+pc}$ and $^5\chi_{p+pc}$ (ref. 28).

The boiling temperature, molar refraction (R_M), V_W and the total path connectivity index of the three orders, $^{1-3}\chi_p = {}^1\chi + {}^2\chi + {}^3\chi_p$, were used as variables in eqn. 2.

TABLE I

RETENTION INDICES AND PHYSICO-CHEMICAL PARAMETERS OF AROMATIC HYDRO-CARBONS

Hydrocarbon[a]	I_{100}^{OV-101}	$t_b(°C)$	R_M	V_W	$^{1-3}\chi_P$
B	663.6	80.10	26.187	48.36	3.8214
MeB	766.4	110.63	31.097	59.51	5.0059
EtB	858.9	136.19	35.763	69.74	6.0616
1,4-DiMeB	867.7	138.35	36.008	70.66	6.1943
1,3-DiMeB	866.6	139.10	35.962	70.66	6.1532
1,2-DiMeB	890.3	144.41	35.803	70.66	6.3373
n-PrB	949.3	159.22	40.453	79.97	7.0884
1-Me-4-EtB	958.2	161.99	40.702	80.89	7.2500
1-Me-3-EtB	955.9	161.31	40.658	80.89	7.2153
1-Me-2-EtB	974.2	165.15	40.450	80.89	7.3102
1,3,5-TriMeB	963.3	164.72	40.819	81.81	7.2632
1,2,3-TriMeB	1015.9	176.08	40.454	81.81	7.6363
n-BuB	1048.1	183.27	45.100	90.20	8.2223
1-Me-3-n-PrB	1043.4	181.75	45.323	91.12	8.2423
1-Me-4-n-PrB	1047.5	183.45	45.343	91.12	8.2769
1-Me-2-n-PrB	1059.0	184.75	45.132	91.12	8.3451
1,3-DiEtB	1040.4	181.10	45.347	91.12	8.2777
1,2-DiEtB	1052.7	183.42	46.411	91.12	8.3047
1-Et-3-n-PrB	1125.8	201.00	49.742	101.35	9.3361
1-Et-2-n-PrB	1134.8	203.00	52.260	101.35	9.3396
1-Me-3-n-BuB	1140.7	206.50	49.971	101.35	9.3761
1-Me-4-n-BuB	1146.1	207.60	50.059	101.35	9.4108
1-Me-2-n-BuB	1154.8	208.60	49.817	101.35	9.4789
1,2,3,4-TetraMeB	1139.2	205.04	45.124	92.96	8.9389
n-PeB	1145.3	205.40	49.735	100.43	9.3258
n-HexB	1243.6	227.35	54.301	110.66	10.4294
PentaMeB	1260.3	232.00	49.681	104.11	10.2038

[a] B = benzene; Me = methyl; Et = ethyl; Pr = propyl; Bu = butyl; Pe = pentyl; Hex = hexyl.

TABLE II

CORRELATION COEFFICIENTS AND STANDARD DEVIATIONS (i.u.) FOR EQN. 2

Series of alkylbenzenes[a]	t_b		R_M		V_W		$^{1-3}\chi_P$	
	r	s	r	s	r	s	r	s
1-Me-2-EtB, 1,2-DiEtB, 1-Et-2-n-PrB	1.000	0.5	1.000	1.5	1.000	0.8	1.000	0.1
B, MeB, 1,3-DiMeB, 1,3,5-TriMeB	1.000	3.3	1.000	1.5	1.000	1.8	1.000	0.2
1,3-DiMeB, 1-Me-3-EtB, 1-Me-3-n-PrB, 1-Me-3-n-BuB	1.000	1.8	1.000	3.0	1.000	2.7	1.000	0.5
MeB, 1,4-DiMeB, 1-Me-4-EtB, 1-Me-4-n-PrB, 1-Me-4-n-BuB	1.000	4.2	1.000	2.3	1.000	2.3	1.000	0.7
B, MeB, EtB, n-PrB, n-BuB, n-PeB, n-HexB	0.999	10.1	1.000	2.8	1.000	2.7	1.000	0.7
1,2-DiMeB, 1-Me-2-EtB, 1-Me-2-n-PrB, 1-Me-2-n-BuB	1.000	1.7	1.000	2.5	0.999	3.5	1.000	1.0
1,3-DiMeB, 1-Me-3-EtB, 1,3-DiEtB, 1-Et-3-n-PrB	1.000	1.8	1.000	1.3	1.000	1.4	1.000	1.1
MeB, 1,2-DiMeB, 1,2,3-TriMeB, 1,2,3,4-TetraMeB, PentaMeB	0.999	7.9	1.000	0.7	1.000	1.3	1.000	1.1

[a] Abbreviations as in Table I.

TABLE III

REGRESSION COEFFICIENTS FOR EQN. 1 FOR ALKYLBENZENES

Form of function	Stationary phase	Coefficients of equation							b	r	s
		a_1	a_2	a_3	a_4	a_5	a_6	a_7			
$I = f(V_w, {}^1\chi, {}^2\chi, {}^3\chi_c)$	Squalane	34.4	−518.5	−381.2	−436.7				125.5	0.997	8.9
$I = f(V_w, {}^2\chi, {}^3\chi_c)$		34.0	−534.9	42.7					132.3	0.998	8.3
$I = f(V_w, {}^1\chi, {}^2\chi, {}^3\chi_c, {}^4\chi_{pc})$		31.2	−497.2	69.1	−486.3	33.3			165.1	0.998	7.2
$I = f(V_w, {}^1\chi, {}^2\chi, {}^3\chi_p, {}^3\chi_c, {}^4\chi_{pc})$		26.6	−447.8	83.7	−412.6	−412.6	−18.9		123.7	0.999	6.1
$I = f(V_w, {}^1\chi, {}^2\chi, {}^3\chi, {}^3\chi_c, {}^4\chi_c, {}^4\chi_{pc}, {}^5\chi_p)$		27.8	−445.8	64.5	78.0	−402.0	−19.7	−59.0	90.4	0.999	4.5
$I = f(V_w, {}^1\chi, {}^3\chi_c)$	OV-101	31.9	−463.6	−355.7					149.9	0.998	8.6
$I = f(V_w, {}^1\chi, {}^2\chi, {}^3\chi_c)$		31.5	−476.2	32.9	−398.3				155.1	0.998	8.2
$I = f(V_w, {}^1\chi, {}^2\chi, {}^3\chi_c, {}^4\chi_{pc})$		27.7	−426.6	69.1	−466.4	45.6			100.0	0.999	5.9
$I = f(V_w, {}^1\chi, {}^2\chi, {}^3\chi_p, {}^3\chi_c, {}^4\chi_{pc})$		23.2	−376.1	78.8	78.8	−394.1	−71.4		157.6	0.999	4.5
$I = f(V_w, {}^1\chi, {}^2\chi, {}^3\chi_p, {}^3\chi_c, {}^4\chi_{pc}, {}^5\chi_p)$		24.1	−374.6	67.8	77.8	−386.0	−6.2	−44.9	132.2	1.000	3.4

CORRELATIONS FOR ALKYLBENZENES

   The physico-chemical characteristics and retention indices of the alkylbenzenes on OV-101 are presented in Table I.

   The results of regression analysis for different values of the parameter x in eqn. 2 are given in Table II. The data obtained show that all the studied parameters can be correlated with retention indices. The equations that include the structural characteristics, in particular the equations containing $^{1-3}\chi_p$, have the highest significance and give the lowest standard deviations of the calculated retention indices. Hence the connectivity index has an advantage over the Van der Waals volume and other parameters.

   The calculated values of V_W and χ for 39 C_6–C_{12} alkylbenzenes[25,26] were used in eqn. 1 for construction of structural models and for the determination of their correlation with the retention indices by solving all possible linear regression equations of the type

$$I = f(V_W, {}^1\chi, \ldots, {}^n\chi_m) \tag{3}$$

where n is the order number of the index and m is the designation of the path or cluster index. The molecular descriptors have the physical meanings that the Van der Waals volume describes solute size only and the connectivity index characterizes its shape.

   The results of statistical processing of multi-factor equations having the highest level of correlation with a successive increase in the number of structure parameters are presented in Table III. The highest level of correlation is provided by structural models which contain both the descriptor V_W and the different order connectivity indices. The additional introduction of V_W into the structural models of molecular connectivity or instead of some connectivity indices increases the significance of the equations and lowers the standard deviations. The correlation level of equations containing only different order connectivity indices does not exceed 0.993–0.995. Therefore, the retention indices calculated by such equations are unsuitable for exact indentifications.

   When evaluating the role of separate molecular connectivity indices, it ought to be noted that in a series of path indices $^1\chi$, $^3\chi_p$, $^4\chi_p$, the descriptor $^3\chi_p$ is the major structural factor which affects the value of the retention indices and the correlation level of the corresponding regression equations (Table IV). When characterizing flexibility of the alkyl chains, one should take into consideration that the index $^3\chi_p$ is closely connected with a number of possible *gauche–trans* rearrangements and the densities of the isomeric alkylbenzenes[29,30] and accounts for the major part of the change in the retention indices. In a number of instances the effect of $^3\chi_p$ on the correlation level considerably exceeds the contribution of the descriptor V_W (Table IV).

   One also ought to note the role of the path-cluster index $^4\chi_{pc}$, whose significance for the description of the structure of polysubstituted benzenes was discussed by Kier[31]. The descriptor $^4\chi_{pc}$ reflects the fine-structure peculiarities of isomeric alkylbenzenes and enters in almost all equations (Table III), its contribution being essential in some instances.

   Hence the relationship between retention and structure of alkylbenzenes is most completely approximated by the seven-factor polynominal which contains connectivity indices of five orders and the descriptor V_W as independent variables.

TABLE IV

INFLUENCE OF THE TYPE OF THE CONNECTIVITY INDEX ON THE CORRELATION
COEFFICIENT OF HYDROCARBONS ON SQUALANE

Hydrocarbons	Form of function	r
Alkylbenzenes	$I = f({}^{1}\chi, {}^{4}\chi_{pc})$	0.963
	$I = f({}^{3}\chi_{p}, {}^{4}\chi_{pc})$	0.981
	$I = f({}^{4}\chi_{p}, {}^{4}\chi_{pc})$	0.923
	$I = f(V_{w}, {}^{1}\chi, {}^{2}\chi, {}^{4}\chi_{p})$	0.971
	$I = f(V_{w}, {}^{1}\chi, {}^{2}\chi, {}^{3}\chi_{p}, {}^{4}\chi_{p})$	0.982
	$I = f(V_{w}, {}^{1}\chi, {}^{2}\chi, {}^{4}\chi_{p}, {}^{4}\chi_{pc})$	0.987
	$I = f(V_{w}, {}^{1}\chi, {}^{2}\chi, {}^{3}\chi_{p}, {}^{4}\chi_{p}, {}^{4}\chi_{pc})$	0.991
Alkylnaphthalenes	$I = f(V_{w}, {}^{1}\chi)$	0.953
	$I = f(V_{w}, {}^{3}\chi_{p})$	0.974
	$I = f(V_{w}, {}^{4}\chi_{p+pc})$	0.995
	$I = f(V_{w}, {}^{5}\chi_{p+pc})$	0.978
	$I = f({}^{1}\chi, {}^{3}\chi_{c})$	0.925
	$I = f({}^{3}\chi_{p}, {}^{3}\chi_{c})$	0.976
	$I = f({}^{3}\chi_{c}, {}^{4}\chi_{p+pc})$	0.989
	$I = f({}^{3}\chi_{c}, {}^{5}\chi_{p+pc})$	0.978

The practical applicability of the equations obtained was checked by elimination
of some retention indices from the bulk, determination of coefficients of new equations
(similar to seven-factor polynomials in Table III) and subsequent calculation of the
retention indices of the excluded hydrocarbons. The data obtained (Table V) indicate
sufficient reliability of the proposed equations to be applied to the prediction of

TABLE V

COMPARISON OF EXPERIMENTAL AND PREDICTED RETENTION INDICES OF ALKYLBEN-
ZENES

Compound[a]	Squalane			OV-101		
	I_{exp}	I_{pred}	ΔI	I_{exp}	I_{pred}	ΔI
B	651.1	656.2	−5.1	663.6	664.9	1.3
MeB	757.9	762.2	−4.3	766.4	769.1	−2.7
EtB	848.7	844.1	4.6	858.9	856.3	2.6
1,4-DiMeB	862.1	861.3	0.8	867.7	866.5	1.2
1,3-DiMeB	864.1	865.5	−1.4	866.6	868.2	−1.6
n-PrB	936.8	934.0	2.8	949.3	946.4	2.9
1-Me-2-EtB	974.2	975.0	−0.8	964.3	965.1	−0.8
1-Me-3-i-PrB	1002.4	1001.8	0.6	1011.9	1011.7	0.2
1-Me-2-i-PrB	1016.7	1017.8	−1.1	1032.3	1031.1	1.2
1-Me-3-n-PrB	1033.8	1035.8	−2.0	1043.4	1042.1	1.3
1-Et-4-i-PrB	1098.4	1099.4	−1.0	1104.9	1112.4	−7.5
1,2,3,5-TetraMeB	1112.6	1113.9	1.3	1110.5	1112.3	−1.8
1-Et-2-n-PrB	1120.2	1119.2	1.0	1134.8	1134.5	0.3
1-Me-3-n-BuB	1129.8	1133.8	−4.0	1140.7	1142.1	−1.4
n-HexB	1230.4	1222.8	7.6	1243.6	1239.1	4.5

[a] Abbreviations as in Table I.

retention indices and to be used for the standardless identification of alkylbenzenes in complex mixtures.

CORRELATIONS FOR ALKYLNAPHTHALENES

The retention indices of fifteen C_{10}–C_{13} alkylnaphthalenes[8,26] were studied. The structural models of these naphthalenes were used for the solution of eqn. 1.

The results of statistical processing of multi-factor equations possessing the highest level of correlation with a subsequent increase in the number of structure parameters are presented in Table VI. The highest level of correlation is provided by a five-factor polynominal of the first power. The equations obtained on HPE have the same high significance as those obtained on OV-101.

The alkylnaphthalenes investigated represent a comparatively narrow series of isomeric hydrocarbons. Therefore, the role of the descriptor V_W is considerably less and its contribution to the retention indices is comparable to that of certain connectivity indices compared with alkylbenzenes.

The path-cluster indices $^4\chi_{p+pc}$ and $^5\chi_{p+pc}$ carry information on the degree of branching of alkylnaphthalenes and make an essential contribution to the retention indices. Table IV gives comparative data on the influence of four types of connectivity indices on the correlation coefficient of the regression equations. It is shown that the above descriptors can be arranged in a series, $^4\chi_{p+pc} > {}^5\chi_{p+pc} > {}^3\chi_p > {}^1\chi$, according to their contribution to the retention indices and their influence on the level of correlation of the corresponding equations. Hence the total connectivity indices of the fourth and fifth orders explain the major part of the variations in the values of the retention indices of alkylnaphthalenes. These indices are sensitive to the positions of the methyl groups on the naphthalene ring.

The path indices $^3\chi_p$ characterize the flexibility of alkyl chains and may be considered as additional fine regulating elements for the retention indices.

The practical applicability of the equations obtained (Table VI) was checked systematically by elimination of the retention indices for some hydrocarbons from the total bulk, determination of new equation coefficients (similar to the five-factor equations given in Table VI) and subsequent calculations of the retention indices of the eliminated compounds with help of the new equations. The data obtained (Table VIII) indicate sufficient reliability of the proposed equations for predicting the retention indices of alkylnaphthalenes on OV-101 and HPE.

The reliability of the proposed equations (Table VI) for the prediction of retention indices was examined on the example of 1-ethylnaphthalene and 2,3,5-trimethylnaphthalene, whose retention indices for the calculation of the correlation equations on OV-101 were not used. The deviations from the experimental values[32] obtained for the retention indices calculated by means of a five-factor polynomial were 5.1 i.u. for 1-ethylnaphthalene and 6.1 i.u. for 2,3,5-trimethylnaphthalene, i.e., the error of the calculated values does not exceed 0.4%.

CORRELATONS FOR ALKYL ARYL CARBAMATES

The retention indices of 27 alkyl aryl carbamates (AAC)[27], whose structural models in connection with eqn. 1 contained V_W and the connectivity indices of the four orders, were studied.

TABLE VI

REGRESSION COEFFICIENTS FOR EQN. 1 FOR ALKYLNAPHTHALENES

Form of function	Stationary phase	Coefficients of equation						r	s
		a_1	a_2	a_3	a_4	a_5	b		
$I = f(V_W, {}^4\chi_{p+pc}, {}^5\chi_{p+pc})$	OV-101	7.1	160.6	−86.3			501.7	0.999	3.1
$I = f(V_W, {}^2\chi, {}^4\chi_{p+pc}, {}^5\chi_{p+pc})$		5.9	42.7	192.6	−135.6		489.6	0.999	2.9
$I = f(V_W, {}^3\chi_c, {}^4\chi_{p+pc}, {}^5\chi_p, {}^5\chi_{pc})$		7.7	48.3	165.2	−166.1	−96.7	506.9	1.000	1.7
$I = f(V_W, {}^4\chi_{p+pc}, {}^5\chi_{p+pc})$	HPE	5.4	280.8	−154.5			827.7	0.998	5.9
$I = f(V_W, {}^2\chi, {}^4\chi_{p+pc}, {}^5\chi_{p+pc})$		3.2	74.7	331.5	−234.6		810.2	0.998	5.1
$I = f(V_W, {}^3\chi_c, {}^4\chi_{p+pc}, {}^5\chi_p, {}^5\chi_{pc})$		5.7	92.3	299.8	−249.8	−192.7	840.5	0.998	4.8

TABLE VII

REGRESSION COEFFICIENTS FOR EQN. 1 FOR ALKYL ARYL CARBAMATES

Form of equation	Group	Coefficients of equation						r	s
		a_1	a_2	a_3	a_4	a_5	b		
$I = f({}^2\chi, {}^4\chi_{pc})$	1	258.1	−1303.0				1063.9	0.999	3.3
$I = f({}^2\chi, {}^3\chi_{p+c}, {}^4\chi_{pc})$		221.1	70.9	−1250.0			1034.2	1.000	1.4
$I = f(V_W, {}^3\chi_c, {}^4\chi_{pc})$		9.8	−1216.0	2024.0			236.1	1.000	0.1
$I = f(V_W, {}^1\chi, {}^3\chi_c)$	2	49.5	−834.5	−1177.0			127.0	0.999	2.4
$I = f(V_W, {}^1\chi, {}^2\chi, {}^3\chi_p)$		16.9	229.1	−131.5	−491.6		−155.4	1.000	0.6
$I = f(V_W, {}^2\chi, {}^4\chi_{pc})$	3	3.8	399.4	−758.8			425.3	0.987	15.7
$I = f(V_W, {}^3\chi, {}^3\chi_p, {}^4\chi_{p+pc})$		5.7	553.1	341.1	−384.0		617.6	0.997	7.0
$I = f(V_W, {}^2\chi, {}^3\chi_p, {}^4\chi_p)$		11.3	−160.9	751.8	−671.6	−482.9	681.8	0.998	6.1

TABLE VIII

COMPARISON OF EXPERIMENTAL AND PREDICTED RETENTION INDICES OF ALKYL-NAPHTHALENES

Compound[a]	OV-101			HPE		
	I_{exp}	I_{pred}	ΔI	I_{exp}	I_{pred}	ΔI
N	1191.0	1189.1	1.9	1502.2	1506.4	−4.2
2-MeN	1293.9	1291.3	2.6	1608.2	1608.1	0.1
1,4-DiMeN	1425.9	1423.1	2.8	1759.4	1755.4	4.0
1,5-DiMeN	1428.0	1429.9	−1.9	1765.8	1764.9	0.9
1,2-DiMeN	1439.7	1435.5	4.2	1776.9	1772.9	4.0
2,3,6-TriMeN	1529.4	1531.1	−1.7	1854.6	1856.9	−2.3

[a] N = naphthalene; Me = methyl.

The regression equations obtained for all 27 AAC are characterized by a low correlation coefficient (0.46–0.50), which can be explained by peculiarities of the interactions of the different functional groups of AAC with the stationary phase. In this connection it is expedient to divide the set of AAC into three groups, each group containing compounds that are similar in structure and the pattern of intermolecular interactions with the stationary phase: group 1, alkyl N-phenyl carbamates with an unsubstituted phenyl radical; group 2, alkyl N-aryl carbamates with different alkyl substituents in the phenyl radical; and group 3, ethyl N-(R-phenyl) carbamates where R = halo or alkoxy.

The results of statistical processing of multi-factor equations which have the highest level of correlation in each group of AAC with a subsequent increase in the number of factors are presented in Table VII. The results demonstrate that the correlation level of the equations increases in the order: group 3 < group 2 < group 1. The number of parameters necessary to achieve an equal level of correlation is lower in the same order. Thus, for the compounds of group 3 the correlation coefficient $r = 0.998$ is obtained by means of the five-factor polynomial of the first power (Table VII), and for AAC in groups 2 and 1 corresponding value is obtained by three- and two-factor equations respectively.

When analysing the composition and nature of the factors in the equations obtained, the predominant role of the cluster indices $^3\chi_c$ and $^4\chi_{pc}$ and of the total index $^4\chi_{p+pc}$, which are present in almost all equations, should be noted. The path index $^2\chi$ has the same essential meaning for compounds of group 3, whose contribution to equations of this group predominates.

Similarly to the alkylnaphthalenes, the contribution of the descriptor V_W to the values of the retention indices is comparable to that of the connectivity indices, but sometimes it is even lower (Table VII). In this case, the descriptor V_W and the path-cluster indices $^3\chi_c$ and $^4\chi_{pc}$ have an opposite influence on the values of the retention indices.

CONCLUSION

Regularities of the gas chromatographic behaviour of alkylbenzenes, alkyl-

naphthalenes and alkyl aryl carbamates may be described by structural models containing the Van der Waals volume and molecular connectivity indices of different levels. The investigations have shown that the role of the descriptor V_W is important for correlations for alkylbenzenes, whereas isomeric alkylnaphthalenes and AAC are differentiated only weakly by this descriptor.

It has been established that in addition to V_W, the path index $^3\chi_p$ makes an essential contribution to the retention indices of alkylbenzenes. The principal contribution to the retention indices of alkylnaphthalenes is made by the total path and cluster indices, $^4\chi_{p+pc}$ and $^5\chi_{p+pc}$.

It is expedient to determine the correlations for separate AAC groups which are characterized by similar structures and intermolecular interactions with the stationary phase. The greatest contribution to the retention of AAC is made by the path-cluster index $^4\chi_{pc}$ and the total index $^4\chi_{p+pc}$.

The equations obtained are applicable to the prediction of the retention indices on apolar stationary phases and for the standardless identification of compounds in complex mixtures.

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