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The use of correlation equations for the prediction of retention parameters in gas–liquid chromatography

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Abstract. The correlations between the retention parameters and the physicochemical properties of sorbates are examined and the possibility of their use for the identification of compounds in gas–liquid chromatography is discussed. It is shown that the chromatographic retention can be most accurately fitted by multifactorial equations based on structural and topological parameters. The bibliography includes 256 references.

I. Introduction

A number of reviews and monographs have been devoted to the problem of the preliminary calculation of retention parameters and the identification of substances in gas–liquid chromatography (GLC).[1–4] At the present time, this topic continues to interest investigators, particularly in connection with the universal chemical analysis system being developed.[5, 6] The methodology underlying such a system involves using a computerised standard reference data bank to derive individual retention parameters and functional relations between the retention parameters and the physicochemical properties of the substances analysed.

Considerable advances have been achieved in qualitative analysis with the aid of so called standard-free identification methods[7, 8] based on the correlations between retention parameters and various physicochemical characteristics of the substances being separated. An advantage of these methods is that they do not require the availability of the postulated components of the test mixture.

The interaction in the sorbate–sorbent system, which determines the chromatographic retention of a substance, is a result of the structural units of the molecule being brought into contact. The mathematical modelling of the retention, which reflects the characteristics of such interactions, gives rise to the possibility of not only identifying the compound but also of predicting the chromatographic behaviour of its molecule as a whole, i.e. of achieving a predictive calculation of retention parameters on the basis of the postulated structural formula.[9–12]

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The correlations between the structure of substances and chromatographic parameters frequently assume the form of linear equations, although other types of functions are also possible: fractional-linear, third degree, etc.[13, 14] The retention parameters used in correlation equations are proportional to the free energy change associated with the chromatographic distribution process. The relations between the structures of the substances separated and their chromatographic parameters can be regarded as an example of the linear free energy relations (LFER).[15]

The correlations between the physicochemical properties of sorbates, obtained mainly on non-polar and weakly polar stationary phases, for which adsorption effects do not exert a significant influence on the retention parameters, are analysed in this review.

II. Dependence of retention parameters on the number of carbon atoms and the molecular mass

A relation of the following type is frequently used in practice for chromatographic identification:

$$R = an + b, \qquad (1)$$

where R are logarithms of the corrected retention time or volume, the specific or relative retention volume, or the retention index, a is a constant characterising the contribution of the interaction energy of a CH_2 group with the stationary phase, b is a constant reflecting the contribution of the interaction of the functional groups with the sorbent to the retention energy, and n is the number of carbon atoms. The validity of Eqn. (1) for homologous series of different compounds has been confirmed in both early[7, 16–18] and later[19–23] studies. A relation of type (1) is characteristic of a wide range of organic substances (Table 1).

A linear relation holds more accurately for non-polar stationary phases, the retention on which is determined by dispersion forces. However, it has been noted[2] that the first members of a homologous series do not obey a linear correlation. This effect is apparently due to the fact that the properties of the methyl (or methylene) group located close to a functional group change under the influence of the latter. It has come to be assumed that the linear relation (1) holds rigorously starting from the third or fourth member of a homologous series, but there have been frequent instances of the breakdown of the linear relation up to the fifth to eighth members[40] and above.[41] Rohrschneider[42] noted the breakdown of linearity in the series of n-alkanes up to C_9,

Table 1. Homologous series of compounds for which the linear relation (1) has been established.

Homologous series	R	Stationary phase	Refs.
C_9-C_{19} *n*-alkanes	$\lg t'_R$	Squalane, phases with cyano-groups	24
C_5-C_8 *n*-alkanes, alkenes	$\lg V_R$	Porapak Q, Polysorbate-2, Polysorb	25
C_1-C_{12} *n*-alkanes	$\lg t'_R$	SE-30, OV-25, Silar 7CP	26
C_6-C_{14} *n*-alkenes	I	PEG 4000, poly(phenyl ether), OV-101, 1,2,3-tris-(2-cyanoethoxy)propane	27–29
n-Alkanes, cycloalkanes, C_4-C_{12} cycloalkenes	I	SE-30	30
C_6-C_{12} aromatic hydrocarbons	I	Squalane, OV-101	31, 32
C_6-C_9 alkylphenols and alkylanilines	I	Apiezon M	8
C_6-C_{10} alkyl- and alkenylpyridines	$\lg V_R$	PEG 1000	33
C_4-C_{10} aldehydes	I	Carbowax 1540	34
C_1-C_{12} aliphatic alcohols and amines	I	Apiezon L, PEG 2000	8, 35
C_1-C_{15} aliphatic amines	I	Apiezon L, Triton X-305, PEG 1000	36
C_2-C_{20} aliphatic amines	I	SE-30	30
Methyl esters of $C_{12}-C_{24}$ aliphatic acids	I	SE-30, OV-225, Silar 5CP	37
Methyl ethers of C_7-C_{17} phenols	$\lg V_g$	Apiezon L, poly(ethylene glycol succinate)	38
C_5-C_{14} esters	I	Squalane, Carbowax 1540	39

while Grigor'eva and Golovnya[43] showed that Eqn. (1) does not hold for any sequence of homologues containing more than 7–8 members. As regards the prediction of retention parameters, the above limitations extend over the interpolation range, the expansion of which leads to an increase in the error of the determination.[44]

The distortion of the linear relation is influenced by the parity of the number of carbon atoms: the free energy of solution increment for the methylene group in n-alkanes with an even number of carbon atoms is greater than in those with an odd number.[3]

The inaccurate determination of the 'dead' volume, the use of methane as the non-sorbable component, and the assumption that its retention volume is zero may also cause deviations from linearity. Reviews[45,46] have been devoted to these questions and to comparing the characteristics of the computational methods for the determination of the 'dead' volume.

In order to take into account the non-linear variation of retention parameters as a function of the number of carbon atoms, various equations have been proposed (Table 2). The majority of them describe the gas-chromatographic parameters of *n*-alkanes. Comparison of the retention parameters calculated by Eqns. (2)–(9) and determined experimentally showed that the highest accuracy of the calculation is achieved on the basis of Eqns. (4) and (8).[53] At the same time the error of the determination of retention indices by Eqn. (8), which is 3–6 units, restricts its application in identification with the use of a computer.[43]

The universal equation (10), describing the gas-chromatographic behaviour of all the members of any homologous series R_nX on stationary liquid phases of different polarity with an accuracy sufficient for the identification of homologues, including the first members, is free from this disadvantage.

It is easy to show that the change in the length of the hydrocarbon chain of the molecule by one CH_2 group (or another group or atom) leads to the corresponding change in the molecular weight of the compound, so that

$$R = aM_S + b, \tag{11}$$

where M_S is the molecular weight of the sorbate.

Eqn. (11), which was already noted by James,[56] has been confirmed in relation to various classes of compounds.[8,21,35,57] It is based on the enhancement of the dispersion interaction with increase in the volume and mass of the molecule and holds most rigorously for homologous series.[58,59] For non-polar systems, this relation is linear[60] and standard deviations of the calculated retention indices are 4–7 units[59] but can be also higher. They can be reduced with the aid of multifactorial equations. Thus the retention indices of 1-haloalkanes calculated by the equation $I = f(n, M_S)$ differ from the experimental values by 1–2 units.[61]

In polar systems, the correlation coefficient for Eqn. (11) is appreciably smaller[62] or this relation does not hold at all.[63]

Table 2. Non-linear equations for the calculation of the retention parameters in GLC as a function of the number of carbon atoms.

Homologous series	Equation	No. of equation	Refs.
n-Alkanes, *n*-alkenes	$\lg V_g = an - n/2 - b$	(2)	47
	$\lg t'_R = an + b\lg(n-4) + c$	(3)	48
n-Alkanes	$\lg V_g = an + b/(n-c) + d$	(4)	49
	$\lg t'_R = an + b\lg n + c\lg(\lg n) + d$	(5)	50
	$\lg V^{rel} = an + bn^2 + cn^3 + d + D\varphi$	(6)	51
n-Alkanes, *n*-alkenes, *n*-alkynes	$\lg t'_R = an + bn^2 + c$	(7)	29
n-Alkenes, amines, sulphides, aliphatic acids, alhehydes, ketones	$I = an + b/n + c$	(8)	36, 37
n-Alkenes, alkyl trichloroacetates	$\lg t'_R = an + bn^2 + cn^3 + d$	(9)	52
n-Alkanes,, amines, alcohols, aldehydes, ketones, sulphides, carbamates, alkylbenzenes	$I = an + b(\lg n)/n + c/[(n-2)^2 + 0.1] + d$	(10)	43, 53–55

III. Correlation between the retention, the vapour pressure, and the boiling point

A linear relation between the retention and the vapour pressure of the sorbate is valid for homologous series:

$$\lg V_g = a \lg p^0 + b. \quad (12)$$

It can be obtained from the fundamental Herington equation and the dependences of the vapour pressure and the activity coefficient on the number of carbon atoms in the molecule.[64]

Eqn. (12) holds over a wide temperature range up to a pressure of several atmospheres and can be used for identification.[3] The correlation improves if a term incorporating the activity coefficients of substances analysed is introduced into Eqn. (12).[4,64]

Dimov and Shopov[11] proposed a more accurate equation for the calculation of the retention indices of hydrocarbons on non-polar phases:

$$I_{p^0,v^0} = 100\frac{\lg(p_n^0 v_n^0/p_x^0 v_x^0)}{\lg(p_n^0 v_n^0/p_{n+1}^0 v_{n+1}^0)} + 100n, \quad (13)$$

where v_x^0, v_n^0, v_{n+1}^0 are the molar volumes of substances x and of n-hydrocarbons containing n and $n+1$ carbon atoms. Since the retention indices calculated by Eqn. (3) differ from the experimental Kovats indices, corrections must be applied in order to convert I_{p^0}, v^0 into I. The error of the calculation for isoalkanes in squalane is then reduced to 1.4 units, but the number of empirical corrections becomes as much as five, which renders the calculation extremely complex and cumbersome.

Relations similar to Eqn. (12) have been found for isoalkanes and cycloalkanes,[65] aromatic hydrocarbons,[32] and the hydrocarbons in petrol [gasoline] fractions.[66]

The linear dependence of retention parameters on the vapour pressure on non-polar phases has been widely used for the solution of the converse problem: the determination of the vapour pressure from GLC data.[13] The boiling points of compounds are most often used for the determination of correlations with chromatographic retention parameters. The simultaneous solution of Eqn. (12) and

$$\lg p^0 = b - aT_b$$

yields

$$R = aT_b + b. \quad (14)$$

Eqn. (14) does not hold rigorously even for homologous series, since the dependence of the boiling point on the number of carbon atoms is non-linear.[3] In homologous series, an increase in the boiling point per methylene group is approximately constant. However, in reality this difference between the boiling points diminishes with increase in the number of carbon atoms, i.e. it depends on the type of homologous series and M_S. Thus the difference between the boiling points for successive C_9-C_{16} n-alkanes decreases from 23.5 to 17.0 °C.[67]

Over a wide range of boiling points, deviations from linearity are observed even for hydrocarbons, especially for the lower members of this series.[3,68] These deviations are most notable in series of polar compounds such as phenols,[69] pyridines, quinolines,[60,70] etc.[71] Table 3 presents a list of homologous series for which Eqn. (14) is valid.

When a two-parameter relation $I = f(T_b, n)$ is used, the linear correlation improves and the predictive power of the computational method for the determination of retention indices increases.[34,84] A similar equation for esters may include the numbers of carbon atoms in the acid and alcohol fragments.[19]

The generalised dimensionless parameter φ, called the retention number, is used for the identification of related compounds:[3,13]

$$\varphi = \frac{\lg V_{g_x} - \lg V_{g_1}}{\lg V_{g_2} - \lg V_{g_1}} = \frac{T_{b(x)} - T_{b(1)}}{T_{b(2)} - T_{b(1)}},$$

where V_{g_x}, V_{g_1}, V_{g_2}, $T_{b(x)}$, $T_{b(1)}$, and $T_{b(2)}$ are respectively the retention volumes and boiling points of the related substances: the unknown substance x and the known substances 1 and 2. In the calculation of φ, it is essential to use standard compounds belonging to the same homologous series as the test substance. When n-alkanes are used as reference substances, the parameter φ acquires the functions of the temperature retention index, which is unambiguously related to the Kovats index. The index φ is independent of the temperature of the analysis and the stationary phase.

Table 3. Homologous series of compounds for which the linear relation (14) has been established.

Homologous series	R	Stationary phase	Refs.
n-Alkanes, n-alkenes, cycloalkanes	I	Squalane	72
C_6-C_{12} n-alkenes	$\lg t_R^{rel}$	SKTFT-100, penta(phenyl ether)	73
n-Alkanes, isoalkanes, cycloalkanes	I	Squalane, dinonyl phthalate	66
C_8-C_{10} isoalkanes	I	Squalane	3, 68
C_5-C_8 cycloalkenes, cycloalkadienes	I	Squalane	74
Aromatic hydrocarbons			
C_6-C_{12}	$\lg t_R^{rel}$	Squalane	75
C_6-C_{11}	I	Squalane, UCON LB-550X, 50HB-280X, tributyl acetylcitrate, PEG-2CM	76
C_6-C_9	I	Dinonyl phthalate, PEG-4000	77
C_6-C_{10}	I	Squalane	78
Chlorobenzenes	I	Apiezon M, OV-210	79
Methyl ethers of phenols	I	Apiezon L	38
C_5-C_8 alkylpyridines	I	n-Tetracosane, squalane, n-dotriacontane, Apiezon L	60
C_9-C_{11} alkylquinolines	I	OV-101, UKON LB-550X	80
Aliphatic amines			
C_1-C_{15}	I	Liquid paraffin, tristearin, PEG-1000, Twin-80, Triton X-305	7
C_1-C_{14}	I	Apiezon M, PEG 2000	8, 35, 81
C_2-C_{12} n-alkyl sulphides, n-alkyl disulphides	I	SE-30, DC-550, diphenylamine, Apiezon M	82
C_3-C_7 aliphatic n-aldehydes, C_2-C_9 ketones, C_2-C_6 esters, C_3-C_9 aliphatic alcohols	I	Squalane, PEG 1540, 29 different stationary liquid phases	19
Aliphatic n-alcohols	I	OV-101, PEG 20M	83

It has been established[85] that the relation between the retention indices and boiling points is most accurately described by an expression similar to the Antoine equation:

$$T_b = A - \frac{B}{I + C}$$

The standard deviations of the boiling points calculated from the retention indices of polar compounds are 3.3 °C on polar stationary phases, 2.3 °C on non-polar phases, and less than 1.1 °C for hydrocarbons.

Using the principle of linear free energy relations, Sojak[86] obtained a modified Hammett equation for the relation between the retention indices of alkylbenzenes and their boiling points:

$$\lg T_{b(a)} = \lg T_{b(t)} - \frac{1}{\rho}\left(\lg \frac{I_t}{I_a} - b\right), \quad (15)$$

where $T_{b(a)}$ and $T_{b(t)}$ are respectively the boiling points of the alkylbenzene and toluene (adopted as the standard), I_a and I_t are the retention indices of the alkylbenzene and toluene respectively, and ρ and b are constants. The maximum deviations of the boiling points calculated by Eqn. (15) do not exceed 0.6 °C and those of the retention index do not exceed 0.6 unit.

The use of the universal equation (10) made it possible to achieve the predictive calculation of the boiling points of members of homologous series of polar organic compounds (such as amines, alcohols, carboxylic acids, and their nitriles) with a high accuracy: the standard deviation of the calculated boiling points T_b did not exceed 2 °C.[87]

The widely used second Kovats rule,[88] based on the similarity of properties, reflects a linear correlation between I and T_b for isomeric compounds on non-polar stationary phases:

$$\delta I = k\,\delta T_b,$$

where δI and δT_b are respectively the differences between the retention indices and boiling points for two isomers and $k = 5$ is a proportionality coefficient.

Further studies showed that k differs from 5 for certain isoalkanes and isoalkenes.[3] Wide ranges of values of k have been found for alkylbenzenes (1.7–8.2)[31, 89] and alkylpyridines (0.8–6.4).[60] For isomeric C_{10}–C_{11} alkylquinolines, k = 3.9–4.2 on OV-101 and increases with increasing polarity of the stationary phases.[57, 90]

An important characteristic is the temperature coefficient of the retention indices dI/dT, which is frequently used for the identification of components.[91] The identification is based on the dependence of the temperature coefficients on the molecular structures of the substances analysed: on the degree of saturation and branching,[92] on the number of carbon atoms,[93] and on the position of the multiple bond.[27, 28] Sojak and coworkers have shown[86, 94] that the temperature coefficients for alkylbenzene vary within comparatively wide limits and reflect the fine structure differences between the hydrocarbons: they are directly proportional to the polarity of the stationary phases and inversely proportional to the symmetry of the molecules and the number of their alkyl substituents.

Relations have been established between the quantities dI/dT and the molecular structures of amines,[8, 35] alkylpyridines,[60] alkylquinolines,[57, 90] alkylphenols,[38] alcohols and ethers,[34] and hydrocarbons.[31, 32, 89, 95]

IV. Dependence of the retention on the molecular refraction and the dipole moment

In systems formed by polar and weakly polar phases, the chromatographic retention is determined by the strength of the dispersion forces, which is proportional to the polarisability of the substances interacting, i.e. to their refractions. It has been shown[96] that the dependence of the logarithms of the retention volumes of substances in a homologous series on the molar refraction is expressed by a linear function:

$$\lg V_g = aR_M + b. \quad (16)$$

Numerous publications indicate that Eqn. (16) is valid for different homologous series of organic substances.[60, 97–99] Thus the correlation coefficient for the equation

$$I = aR_M + b$$

reaches 0.999–1.000 for the homologous series of hydrocarbons on non-polar and weakly polar phases with a standard deviation of 0.5–2.0 units. For cycloalkanes, the analogous data are 0.990–0.997 and 3.4–4.4 units respectively.[98] The impairment of linearity for cycloalkanes is apparently associated with the manifestation of the effect of intramolecular shielding.

In order to improve the correlation, the specific and molar refractions are frequently used in two-parameter equations in combination with T_b,[76, 77, 99, 100] the dipole moment,[101] or the Hammet constant.[102]

Multiple correlation equations including the molar refraction and the refractive index as independent variables are used for the description of various mechanisms of the intermolecular interaction.[74, 76, 103]

Equations of type (16) make it possible to determine the molar refractions from GLC data with a high accuracy.[104, 105] Thus the average value of R_M for *n*-pentylbenzene, calculated from five equations for different polyester phases, is 50.00, while the value found from familiar formulae using the experimental densities and refractive indices is 49.96.[98]

According to the theory of intermolecular interactions, the dipole moments of substances exert a direct influence on their retention in GLC.[56] The retention indices of alkyl halides are related to the dipole moments as follows:[106]

$$\Delta I_{130} = 6\Delta R_M + 50\mu_{C-X},$$

where ΔI_{130} is the difference between the retention indices on polar and non-polar stationary phases at 130 °C, ΔR_M is the difference between the refractions of the C–X and C–H bonds (X = halogen), and μ is the dipole moment of the C–X bonds.

Franc[107] established a linear relation between the relative retention times and the dipole moments of isomeric alkylphenols, aromatic amines, and nitro-compounds:

$$\lg V^{rel} = a\mu + b. \quad (17)$$

It is noteworthy that the dipole moment enters into Eqn. (17) with an exponent of unity. This conflicts with the equation for the orientation interaction energy.[108] At the same time, the majority of compounds are characterised by having a quadrupole moment as well as the dipole moment.[109] The factors listed are the cause of the appreciable deviations from linearity when Eqn. (17) is used.[62, 109, 110] Therefore Eqn. (17) holds only for a limited number of compounds belonging to separate homologous series.[71, 78] The replacement of μ by μ^2 in Eqn. (17) makes this relation valid for the estimation of the orientation and inductive interaction energies.

Sakharov[111] suggested that the difference between the retention parameters of two substances having equal molar refractions be determined as follows:

$$RT\Delta \lg V_g = \frac{2}{9}\frac{\Delta\mu^2}{r^3}\left(1 - \frac{1}{\varepsilon}\right), \quad (18)$$

where $\Delta\mu^2$ is the difference between the squares of the dipole moments of the sorbates, r is the molecular radius, and ε the dielectric constant of the solvent. The requirement that the molar refractions are equal is stipulated to eliminate the effect of the electronic polarisability.

Eqn. (18) makes it possible to estimate the dipole moments of substances from GLC data with a greater accuracy than Eqn. (17). In the derivation of Eqn. (18), a simplified model of the interaction of the sorbates and the stationary phase, which does not take into

account the mutual polarisation of two molecules, was used. According to Onsager,[112] when account is taken of such polarisation, the following relation should hold:[113]

$$RT \lg V_g = \frac{\Delta\mu^2}{r^3} \frac{\varepsilon - 1}{2\varepsilon + 1}. \quad (19)$$

It is widely used to characterise the intermolecular interaction in various systems.[113-115]

In the multiple regression equations employed, the dipole moment functions as a descriptor of the polarity of the solute.[35,62] Apart from the dipole moment, such equations include the molecular weight, the sum of the steric factors,[62] the molar refraction,[116] the number of carbon atoms, the ionisation potential, the sum of the steric factors,[35] the molecular connectivity index,[117,118] and topological, electronic, and quantum-chemical parameters.[119,120] the correlation coefficients for the proposed equations are fairly high, amounting to 0.740–0.975 on polar phases and to 0.940–0.999 on non-polar phases.

At the same time, the use of the dipole moment of the molecule for the description of the intermolecular interaction does not correspond to the real nature of the orientation interaction.[121] It is known that specific interactions between the molecules of sorbates and the stationary phase depend to a greater extent on the local polarity of these molecules than on the overall dipole moment.[119-122] The electronic topological index (ETI) has been proposed for the quantitative description of the differences between the polar properties of sorbates.[123] It is calculated by the summation of the absolute differences between the excess charges on all the atomic pairs of the given molecule divided by the squares of the corresponding interatomic distances. The correlation equations based on the ETI have a high level of statistical significance for chromatographic parameters obtained on both non-polar and polar stationary phases.

Among other parameters associated with the energy characteristics of sorbates and used in correlations, mention should be made of the electronic polarisability,[13,124] the ionisation potential,[60,98,125,126] the diamagnetic susceptibility,[98] the electron density in molecules,[127] and the resonance energy of the π-electron system.[128]

V. Relation between the retention and the molar volume of the sorbate

The dependence of the retention indices on the molar volume follows from Eqn. (13), which has been used to predict the retention indices of different hydrocarbons.[129] It has been shown[64,131] in relation to alkylsilanes,[130] alcohols, hydrocarbons, and their derivatives that the relation between the retention parameters and the molar volumes of sorbates is linear:

$$I \text{ (or } \lg V_g) = aV_M + b. \quad (20)$$

The validity of Eqn. (20) has been confirmed for short homologous series of aromatic hydrocarbons (r = 0.999 and above) but for the series of C_6–C_{11} alkylbenzenes the correlation coefficient was found to be only 0.88 on squalane and 0.77 on PEG-20M.[99] The correlations considered can be improved with the aid of two- and three-parameter equations including the boiling point and the specific refraction together with V_M as independent parameters.[76,77] The correlation coefficient for such an equation reaches 0.998 on polar stationary phases and more than 0.999 on non-polar ones.

Other physical properties of sorbates which have found applications in correlations include the heat and energy of formation,[13] surface tension,[64] density,[64,68,97,132] viscosity,[133] and heats of crystallisation, evaporation, and combustion.[134,135] Since such characteristics have been determined for a small number of compounds, the possibility of predicting the retention parameters on their basis is extremely limited.

VI. The retention parameters and the principle of linear free energy relations

The interaction of a substance with the stationary phase, determined by the free energy change, can be described by the Hammett equation:[136]

$$\lg \frac{R}{R_0} = \rho\sigma, \quad (21)$$

where R and R_0 are the retention parameters of the given and standard compounds, their ratio being a measure of the free energy change on passing from the standard component to the given component within the limits of the homologous series investigated, σ is the inductive constant of the substituent which serves as a quantitative characteristic of the effect of the substituent on the electron density at the given centre, and ρ is a constant characterising the stationary phase.

The linear relation between the retention parameters of aromatic hydrocarbons and the Hammett constants of stationary phases was first noted by Araki and coworkers and by Nabivach and coworkers[137-140] and was then discovered for a whole series of similar systems.[141,142] This relation was subsequently used to characterise the selectivity of solvents—with the aid of the ratio of the activity coefficients of the sorbates.[143]

The application of the Hammett constants proved to be extremely useful when there is a significant contribution by the specific interaction forces (for example, by the donor–acceptor bond) to the overall intermolecular interaction energy. The series of correlations

$$\lg \frac{R}{R_0} = a\sigma + b$$

(σ is the Hammett constant for the corresponding substituent in the sorbate molecules) have been established for derivatives of phenol, aniline,[144-147] methyl benzoates,[145] alkylbenzenes,[148,149] and nitrobenzenes.[150]

The Taft equation has come to be widely used for the description of the characteristics of intermolecular interactions:[151]

$$\lg \frac{R}{R_0} = \rho^*\sigma^*, \quad (22)$$

in which the parameters R_0, ρ^*, and σ^* are analogous to the corresponding quantities in Eqn. (21). It is assumed that the constant σ^* characterises the purely inductive polar effect of substituents. The linear relation based on Eqn. (22) has been demonstrated for series of alkylbenzenes,[98,149] haloalkanes, halo-derivatives of epoxy-compounds, ethers,[115,152] ethoxyalkanes, amines, alcohols,[153] and alkylquinolines.[57,90]

A method has been proposed for the determination of the induction constant of the methyl group (arbitrarily assumed to be zero) for which the principle of the additivity of the change in the quantity σ^* corresponding to a change in the length of the alkyl group of alkylbenzenes per methylene group holds under GLC conditions.[98] An experimental test confirmed the legitimacy of such calculation of σ^* for the methyl group based on the correlation with the retention indices for different series of alkylbenzenes.

A complex equation has been proposed for the calculation of the retention indices of aniline, phenol, and pyridine derivatives:[154]

$$\Delta \lg V_N = \rho_I\sigma_I + \rho_R\sigma_R + \rho_E\sigma_E,$$

where σ_I, σ_R, and σ_E were derived from literature data with the aid of factorial analysis and were found to be close to the corresponding Taft induction and resonance constants.

The Taft equation for the estimation of the steric effect of substituents[151]

$$\lg \frac{R}{R_0} = \delta E_S, \quad (23)$$

where E_S are the steric constants of the substituents, can be used to characterise the quantitative measures of the steric effects of individual groups in the vicinity of the reaction centres of molecules, in the separation of polar compounds on polar stationary phases. Experimental data have shown that the Taft[57,90,149] and Palm[57,90,155] steric constants as well as their sum[62,102] can be used with equal success in equations of type (23).

In order to increase the correlation coefficient for Eqn. (23) for a series of aromatic hydrocarbons containing branched substituents (for example, butylbenzene isomers), a corrected Palm constant has been proposed:[98]

$$E^0_{S_{cor}} = E^0_S - \varphi,$$

where E^0_S is the Palm steric constant and φ is the contribution of the φ-interaction arising between the groups of the substituent linked directly.[15] The use of $E^0_{S_{cor}}$ instead of E^0_S increases the correlation coefficient of Eqn. (23) for butylbenzene isomers from 0.87 to 0.99.

By combining Eqns (22) and (23), we obtain the Hammett–Taft equation, which makes it possible to describe more complex types of intermolecular interaction[156,157] and to estimate quantitatively the role of each effect.

The Hammett–Taft equation has been improved by French investigators,[153,158] who proposed the following relation:

$$\lg t'_R = \rho^*\delta^* + \delta E_S + h(n_H - 3),$$

where n_H is the number of hydrogen atoms at the carbon atom in the α-position relative to oxygen. Assessment of the resulting coefficients showed that the contribution of E_S is much smaller than the contributions of the remaining terms of the equation, which can be rewritten in the form

$$\lg t'_R = \rho^*\delta^* + h(n_H - 3).$$

The application of this equation to a series of oxygen-containing compounds yielded satisfactory results.

VII. The use of the principle of the additivity of properties for the prediction of retention parameters

A general relation for the calculation of the chromatographic retention, based on the additivity of the contributions by structural fragments, has been proposed by Berezkin and coworkers:[159,160]

$$R = \sum_{ij}^{K} n_{ij}C_{ij} + C_0, \qquad (24)$$

where C_{ij} is the contribution of a particular structural fragment (atoms, a group of atoms, bonds) to R, and n_{ij} is the number of structural fragments in the molecule. Bonds were selected as the computational structural fragments taking into account the immediate environment. If more distant environment is also taken into account, it is possible to obtain more accurate results.

The simplest expression for the additivity rule—Eqn. (1)—is a special case of Eqn. (24). Eqns (11), (14), and (20) are also special cases of this kind.

The principles formulated by Berezkin have found applications in the predictive calculation of retention parameters in accordance with an additive scheme by the summation of increments corresponding to subtypes of bonds between carbon atoms[3,161] or functional groups.[162]

The additivity of the retention characteristics considered logically presupposes also the additivity of the retention indices,[162] whose calculation is based on the principle of the additivity of the intermolecular interaction energies for individual groups of molecules.[106]

The increments in the differences between the retention indices, measured on stationary phases of different polarity and reflecting the specific interaction between the test molecules and the stationary phase, are also additive.[163–166]

The functional retention index proposed by Swoboda[167] reflects the dispersion and specific interactions of the functional group of the sorbate with the sorbent:

$$H_X = I_{R-X} - I_{R-H},$$

where X is the functional group and R–H the homomorphic n-alkane with the same number of carbon atoms. The functional group is understood not only as a group containing a heteroatom but also as any structural group differing in its multiple or aromatic bond or in the arrangement of carbon atoms in space.

Schomburg[9] proposed that the quantity H be called the homomorphy factor and showed that it is extremely sensitive to the characteristics of the fine structure of the molecule.[168]

Andersons and coworkers[8,35] introduced the concept of two homomorphy factors: H_H describes the effect of the substitution of a hydrogen atom by a functional group and H_C describes the effect of the substitution of a carbon atom by a heteroatom or a group of atoms.

Among compounds for which the values of H have been determined and the corresponding correlations with the structure have been established, mention should be made of cycloalkanes, cycloalkenes, cycloalkadienes,[93] alkylbenzenes,[20,89,169] alkylnaphthalenes,[170] alkylpyridines,[60] amines, alcohols, and ethers.[8,35]

Extensive experimental data on the increments for various functional groups or individual fragments, used in accordance with Eqn. (24) for the predictive calculation of retention indices and for the identification of components of complex mixtures, are available in the literature.[171–173]

The principle of additivity breaks down when the structural fragments of the molecule are close to one another, on passing from unbranched to branched compounds, and with increase in the polarity of stationary phase and in the capacity of the functional group for specific interactions.

The non-additivity of the retention indices and their increments in homologous series is also indicated by data in numerous publications.[174,175] Correction coefficients are usually introduced in such cases or one calculates second-order increments, taking into account the positions and interaction of functional groups, the nature of the bonds in the molecule, steric factors, and other effects of substitution and the environment.

The causes of non-additivity and procedures for the reliable prediction of retention indices based on allowance for the non-identity of the energy contributions of identical alkyl groups have been described in detail.[179–185]

One of the causes of the breakdown of additivity is the presence in the molecule of a heteroatom or a functional group, the degree of shielding of which by neighbouring alkyl groups affects appreciably the specific forces of the interaction of the test substance with the stationary phase. Linear relations for such compounds (alkylphenols, alkylpyridines, alkylquinolines, alkylanilines, etc.) are therefore characterised by a low correlation coefficient. In order to take into account the shielding effect, the entire set of compounds (for example, alkylpyridines) can be usefully divided into three groups: alkylpyridines with a non-shielded nitrogen atom, i.e. with alkyl groups in the 3-, 4-, and 5-positions, alkylpyridines with one alkyl group in the *o*-position relative to the nitrogen atom, and alkylpyridines with two alkyl groups in the 2- and 6-positions.[165] Such subdivision is based on the change in the π-electronic charges on the reaction centre under the influence of the alkyl groups introduced into the molecule. This factor is responsible for the linear variation of the basicity of alkylpyridines as a function of the groups indicated, which makes it possible to represent the dependence of the retention indices on the dissociation constants of alkylpyridines by three equations, whose correlation coefficient is 0.995.

The system for the predictive calculation of retention indices developed by Takacs and coworkers[186-188] provides for the use of not only the properties of the pure sorbates but also of the characteristics of their interaction with the stationary phase:

$$I = I_a + I_b + I_i,$$

where I_a is the contribution of atoms, I_b the contribution of bonds, and I_i the contribution of the interaction in the sorbate and the stationary phase.

The Takacs system is based on the separate determination of all the factors responsible for the chromatographic retention of the test substance; its undoubted advantage is the use of molecular constants instead of empirical characteristics or sorbates such as the boiling point, the vapour pressure, and the molar refraction. At the same time, the semiempirical nature of the determination of the components of the index and the need to calculate a large number of empirical parameters give rise to considerable difficulties in the practical application of this system.[189]

VIII. Calculation of retention parameters with the aid of structural and topological parameters

The effect of molecular size on chromatographic retention was first noted by Hively and Hinton,[92] who concluded that the quantity dI/dT increases with increase in the cross-sectional area of the isoalkane molecule.

Similar results were obtained by Littlewood[190] for *n*-alkanes and their derivatives, whose retention is proportional to the surface area of the molecules calculated with the aid of a computer.

Altenburg[3,191] developed a method for the determination of the retention indices of hydrocarbons and their derivatives based on the correlation with the square of the molecular radius:

$$I = I_0 + bM_S d + \frac{c\overline{R^2}}{a_1^2},$$

where d is the density of the hydrocarbon, I_0 a constant which depends on M_S, $\overline{R^2}$ the mean square molecular radius, a_1 the length of a carbon–carbon single bond, and b and c are constants of the equation.

More accurate results were obtained by using equations including, together with $\overline{R^2}/a_1^2$, the boiling point:[3,68]

$$I = a + b(T_b - 273.15) + \frac{c\overline{R^2}}{a_1^2},$$

$$I = a + b(T_b - 273.15) + C(T_b - 273.15)^2 + \frac{D\overline{R^2}}{a_1^2} + E\left(\frac{\overline{R^2}}{a_1^2}\right) + Fd + Gd^2.$$

The error of the calculated retention indices of isoalkanes varies in the range 0.3–5.5 units. For example, equations of the following type are valid for the homologous series of alkylbenzenes:

$$I = f\left(\frac{\overline{R^2}}{a_1^2}\right)$$

with a correlation coefficient of 0.994 and above.[192,193]

Correlation equations relating the retention index to the shape parameters of the molecules, which have been calculated on the basis of the van der Waals radii of the hydrogen atom for polycyclic aromatic hydrocarbons[194] or the van der Waals surface areas for polychlorinated dibenzofurans,[195] have been proposed.

Correlations based on the van der Waals volumes of sorbate molecules V_W have come to be widely used. Hammers and De Ligny[196] already showed that the thermodynamic functions of solution in squalane, calculated from the retention volumes, are linearly related to V_W for hydrocarbons in different homologous series.

Linear relations between retention indices and the van der Waals volume have been observed for the homologous series of alcohols, ketones, aldehydes, ethers,[197] *n*-alkanes and isoalkanes,[198] ketone derivatives,[21] alkylbenzenes[99,105,199] and alkylphenols.[200] The correlation coefficients of such equations are 0.999–1.000 for hydrocarbons on non-polar phases and 0.994–1.00 for other compounds. When the above relation is applied not to short homologous series but to the entire set of isomeric compounds (for example, alkylbenzenes), the correlation coefficient falls as a function of the polarity of the stationary phases to 0.88–0.98. The level of correlation can be improved by combining V_W with characteristics of sorbate such as the boiling point, the refractive index, and the specific refaction within the framework of three- and five parameter equations.[76,79,99,197]

When correlations in the structure–retention system are considered, various methods for the conversion of molecular structures into unique characteristic structural descriptions, expressed by numerical indices, are very promising. For this purpose, one uses chemical graph theory, according to which the chemical structural formula of a compound is expressed by a mathematical graph. The mathematical graph describes abstract vertices connected by faces. Each molecular graph can be represented either by a matrix, or by a polynomial, or by numerical index (topological index).[201] The topological index contains information about the size and shape of the molecule, about the connections between atoms and structural groups, and about their mutual disposition.[202]

More than 40 different topological indices are known at the present time. An approximate classification, the characteristic principles of the derivation of topological indices, and their realistic possibilities as a means of describing chemical structures when correlations of the structure–property type are considered have been described in detail in a number of reviews.[201-208a]

The topological index W proposed by Wiener[209] for the comparison of carbon skeletons is defined as the sum of the C–C bonds between all the pairs of carbon atoms in the molecular graph:

$$W = \frac{1}{2}\sum_{ij} D_{ij}.$$

The smaller this number, the more compact the corresponding structure.

Correlations between the Wiener index and the chromatographic retention parameters of various hydrocarbons have been described.[105,199,210-212] A disadvantage of the Wiener index is the fact that part of the information contained in the distances matrix is lost during the summation of its elements. This explains the finding that the values of W referring to different isomers frequently overlap. It has been established that, compared with W, a higher level of correlation is ensured by the molecular connectivity index.[105,199,212]

The concept of the connectivity index, which is one of the most popular topological indices in theoretical chemistry, was introduced by Randic.[213] Later this method of topological analysis was used as a basis of the molecular connectivity system.[214]

Molecular connectivity constitutes a topological description of the molecular structure and represents mathematically coded information about the size of the molecule, the degree of its branching, cyclisation, and unsaturation, and about its content of heteroatoms. The first-order connectivity index is most common:[214]

$$^1\chi = \sum_{q=1}^{K} (\delta_i \delta_j)^{-1/2}, \qquad (25)$$

where δ is the difference between the numer of valence electrons and the number of hydrogen atoms connected to the given atom, i and j are the atoms of the molecule formally connected by the bond under consideration, δ_i and δ_j are the values of δ for two

atoms involved in a bond q, and K is the total number of bonds in the molecule.

The second-order to fourth-order and higher-order connectivity indices are calculated similarly. These take into account the numbers of two, three, four, and more of neighbouring bonds respectively. In Eqn. (25), the first-order connectivity index takes into account the pair interactions of neighbouring atoms in the molecule. A disadvantage is that it does not distinguish the *m*- and *p*-isomers of aromatic compounds. Higher-order connectivity indices, taking into account not only the nearest pair interactions but also remote interactions between atoms in the molecule, ensure a more complete description of the structural features of the test compounds.

Thus molecular connectivity is a fundamental parameter and expresses structural information in the form of a weighted sum of all the types of bonds in the molecule. Compared with other indices, the molecular connectivity model is more flexible, since it makes it possible to relate both general and local structural properties of molecules.

The application of connectivity indices in GLC in order to establish the sorption-structural correlations for different compounds has proved especially fruitful.[77,100,215–221] Table 4 presents data on the correlations based on connectivity indices. A significant advantage of this index compared with the Wiener index is the possibility of describing a compound with polar functional groups. Although a high level of correlation is observed mainly on non-polar phases, it does not reduce the practical value of the proposed equations.[76,239–242]

The application of multiparameter equations, including, apart from the connectivity indices of different orders, also other physicochemical constants of sorbates (the number of carbon atoms, the boiling point, the molar refraction, the dipole moment) makes it possible to increase the correlation coefficient of the equations and to reduce the standard deviation.[241,243] It has been concluded that satisfactory results for compounds of different classes are obtained when a multiparameter equation of the following type is used:[105,199,200]

$$I = f(V_w, {}^1\chi \ldots {}^n\chi_m), \qquad (26)$$

where n is the order of the connectivity index and m the designation of the chain or branching index. In Eqn. (26) the van der Waals volume describes the size of the solute and the connectivity indices of different orders characterise the fine structure features of its form. A close relation has been noted[244] between the indices obtained in accordance with graph theory and by quantum-chemical methods.

Eqn. (26) has been successfully tested for alkylbenzenes and alkylarylcarbamates,[105,199,245] alkylphenols,[200,246] alkylquinolines,[247] aliphatic alcohols,[248] and alkylanilines.[249] The correlation coefficients of the above equations are 0.996–1.000 and the standard deviations are 0.5–8.0 units.

The program packs developed for the calculation of connectivity indices[250–252] and also the combined program for the determination of sorption–structure correlations on the basis of topological indices[253] greatly facilitate chromatographic identification and permit its automation using computers.[2,254]

Another topological system (DARC)[255] involves the arbitrary specification in each molecule of a focus (the given functional group) and its environment—the first, second, third, and subsequent spheres. The reliability and accuracy of the calculations increase with increase in the number of surrounding spheres taken into account. This leads to an increase of the prespecified empirical parameters for the calculation, whose number can reach 2000 and more.[256]

Despite the complexity of the calculations and the large amount of the information used, the accuracy attained in the determination of the retention indices varies within wide limits (3–48 units). Comparison with other computational methods showed that the DARC system has no special advantages and its use for the prediction of the retention parameters involves considerable difficulties.[2]

Analysis of the studies examined shows that the simplest correlations between chromatographic retention and the physicochemical properties of sorbates can be used for a homologous series of compounds in order to characterise their retention on non-polar stationary phases. However, the prediction of the retention parameters is then rather difficult, since physicochemical properties have been determined for a limited number of substances.

Table 4. Characteristics of the correlation equations based on connectivity indices.

Compound	Equation	Stationary phase	Correlation coefficient	Standard deviation	Refs.
n-Alkanes, isoalkanes	$I = a^1\chi + b$	Squalane	0.994	17.3	198
	$\lg t_R^{rel} = a^1\chi + b$	Dimethylsulpholan	0.996	0.1	222
Alkylbenzenes	$I = a^1\chi + b$	Squalane, SE-30	0.999–1.000	–	223
Alkylnaphthalenes	$I = f({}^1\chi \ldots {}^5\chi_p)$	Hepta(phenyl ether)	0.998	4.8	224
Polycyclic aromatic	$I = a^1\chi + b$	SE-52	0.996	8.8	225
hydrocarbons (PAC)	$I = a^1\chi + b$	0V-101	0.998	36.9	226
Nitro-derivatives of PAC	$I = f({}^0\chi \ldots {}^5\chi_p)$	SE-52	0.999	2.3	227
Chloroalkanes	$I = f({}^1\chi, {}^5\chi_p, {}^5\chi_{pc}, {}^6\chi_p)$	PEG-20M	1.000	–	228
Chlorobenzenes	$I = f({}^1\chi, {}^4\chi_{pc})$	SE-30	0.988	–	229
Chlorobiphenyls	$\lg t_R^{rel} = f({}^1\chi, {}^4\chi_{pc}, {}^5\chi_p)$	SE-54	0.999	0.006	230
Alkylpyridines	$I = f({}^0\chi \ldots {}^5\chi_{pc})$	0V-1	0.996–0.999	3.6–8.4	231
Nitrogen-containing heterocycles	$I = f({}^1\chi, {}^4\chi_{pc}, {}^5\chi_p, {}^6\chi_p, {}^6\chi_{pc})$	0V-1	0.960	54.0	232
Alkylpyrimidinone derivatives	$I = a^1\chi + b$	0V-1	0.970	–	233
Cyclic methyl esters and alcohols	$I = a^1\chi + b$	SE-30	0.952	32.2	234
Aliphatic alcohols	$I = a^1\chi + b$	Squalane	0.950	–	235
	$I = a^0\chi + b^1\chi + c$	Squalane	0.994	–	236
Esters	$I = a^1\chi + b^4\chi_p + c$	Squalane	0.996–0.998	–	237
Ethers	$I = a^1\chi + b$	Squalane	0.968	–	236
5,5-Disubstituted barbiturates	$I = a^1\chi_N + b$	SE-30	0.996	–	238

Correlation equations taking into account the deviations from additivity in the intermolecular interaction energy [in particular the universal equation (10)] as well as equations based on the structural and topological parameters of compounds (for example, the van der Waals volume and the connectivity indices) are more reliable and promising. Such sorption–structure correlations can be used in schemes for the automatic identification of complex mixtures with the aid of computers.

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