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The effect of alternation in chromatographic retention relationships

M S Vigdergauz, E I Petrova
Samarskoe State University

ABSTRACT. The effect of the alternation of the chromatographic retention values has been examined for homologous series of sorbates and stationary phases (the even–odd effect) and for other series formed by the successive addition of identical functional groups to the repeating fragments of an aliphatic molecule or ring, as well as by the displacement of functional groups or alkyl groups along a chain or a ring. Particular attention has been paid to the manifestation of this effect when liquid-crystalline stationary phases are used. It has been shown that the diffference in the concentrations of given substances in natural materials may be partly due to the alternation of the sorption characteristics.

The bibliography contains 70 references.

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I. Alternation of the physicochemical characteristics of homologues

In the study of the regularities of the change in the physicochemical properties of substances which are members of homologous series, attention is drawn to the role of the structural factor determined by the characteristics of the configuration of molecules with even and odd numbers of carbon atoms.[1] As a consequence of this influence, the relationship between the physicochemical characteristics and the number of carbon atoms z is given by a zigzag curve, that is alternation of the quantities being studied, depending on the parity of z, is observed.

The influence of the parity of z was first revealed in the study of the regularities of the change in the melting point in the homologous series of n-alkanes.[2,3] The relationship between the melting point and the number z was found to be different for the even and odd homologues. A similar effect was later observed for the aliphatic acid series.[4] Data have been published[5] on the effect of alternation in the change in the melting points and solubilities of dicarboxylic acids. The values of the melting points and solubilities of the numbers of the series with odd values of z are higher than those for the even homologues.

For liquid crystals, the effect of alternation is revealed not only by the melting points but also by the temperatures of other phase transformations: smectic–nematic and nematic–isotropic liquid.[6–11] In addition, in the nematic phase of N-(4-alkoxybenzylidene)-4′-toluidine specimens oriented by a magnetic field, an even–odd effect was detected in the temperature dependence of the parameters of the orientational ordering.[11]

Published data[4,12–15] and their own data were used by a group of authors[16,17] to study the regularities in the influence of the parity of z on the values of the dipole moments, refraction, heats of crystallisation, refractive indices, and size of the crystal cells of aliphatic acids, their methyl esters, and the dimethyl esters of dicarboxylic acids. It was later shown[18] from published data[12,19–22] that a fairly clearly defined alternation of such characteristics as the melting point, density, refractive index, dipole moment, and even boiling point is observed for homologous series of alkylamines, alkylbenzenes, ketones, and esters of carboxylic acids.

One of the possible factors responsible for the alternation of the physical properties of substances (such as the melting point or heat of fusion) is apparently the nature and stability of the packing of the molecules in the crystal.[23] The stability of the packing of the molecules in the crystal in turn depends on their geometry. For example, X-ray diffraction shows that the zigzag chains of the molecules of saturated non-branched hydrocarbons in the crystal are arranged parallel to one another, and that the "convex" parts of one chain enter the "dents" in the other. The physical properties of these substances depend on the parity of the number of carbon atoms, since the symmetry of the individual molecules influences the way in which one layer of molecules in the crystal is superimposed on another. Molecules with an odd value of z have a plane of symmetry passing through the central carbon atom, and the terminal methyl groups are directed in the same direction relative to the axis of the molecule. A chain with an even number of carbon atoms does not have this plane of symmetry, but acquires a centre of inversion, situated between the two central carbon atoms. The terminal methyl groups in these molecules are directed in different directions with respect to the axis of the molecule. This difference in the arrangement of the methyl groups is responsible for the difference in the packing of the layers of molecules.

On crystal formation, hydrocarbons with an even value of z are arranged in such a way that each layer repeats the previous layer (with a slight sideways displacement), whereas in the crystals formed by hydrocarbons with an odd value of z, every second layer has the same arrangement of molecules.

Increase in the chain length eliminates the advantage of one type of packing over another, and for hydrocarbons the even–odd effect gradually decreases, disappearing completely when the number of carbon atoms is sufficiently large.

Similar arguments can be used to explain the even–odd effect in carboxylic and dicarboxylic acids.

II. Alternation of the gas-chromatographic retention values in homologous series of sorbates (even–odd effect)

The possibility of the effect of alternation appearing in the change in the temperatures of the phase transformations in liquid crystals is evidently related to their structural ordering in the solid and liquid states. Since the chromatographic characteristics are also related to the phase transformations, the changes in these characteristics should also show the effect of alternation. The probability of this is greater if the liquid phase has a fairly rigid structure. Kovats[24] initially determined the retention index by a logarithmic interpolation based on the logarithms of the retention volumes of the n-alkanes of the even series, but since the alternation effect was not detected, this was later recognised as unnecessary, and the interpolation began to be carried out on the basis of the retention characteristics of neighbouring n-alkanes.

In the subsequent development of chromatography, when highly efficient columns were introduced (this increased considerably the sensitivity of the determination of the retention characteristics), it was established that the relationship between the retention values and the number of carbon atoms in the molecules of sorbates in a homologous series, previously assumed to be linear, often shows deviations from linearity.[25–29] These deviations may be due to either anomalies in the properties of the sorbates or the corresponding sorption properties of the stationary phases. Detailed study of this question established that the deviations from linearity are related primarily to the characteristics of the molecular structure of the first members of the homologous series and are also determined by the non-constant nature of the increment of the repeating fragment of the molecule. These deviations can be seen particularly clearly when polar sorbates and(or) polar stationary phases are used.

The authors cited[29] also showed that for different stationary phases the difference between (ratio of) the retention values in the series of n-alkylbenzenes and n-alkylcyclohexanes is greatest for the n-propyl-substituted/ethyl-substituted pairs (a similar relationship was found for such physicochemical characteristics as the dielectric constant and surface tension). Sojak and co-workers[30] established that the n-propylbenzene/ethylbenzene pair also has the smallest value of the increment in the retention index on a column containing squalane. This effect was later called the "propyl" effect.[31]

The importance of the parity of z was a factor influencing the retention of homologues was first revealed[32] in a study of the n-alkane–polyethylene glycol system. An experiment carried out on a highly efficient capillary column showed that the relationship between the retention and the number z is given by a broken line, that is alternation of the chromatographic retention values is observed on going from an even to an odd member of the homologous series. Thus strictly speaking this relationship should be represented by two curves, one corresponding to even values of z and the other to odd values. Two anomalous effects, namely the "propyl" effect and the even–odd effect, are shown simultaneously by data on the retention of alkylbenzenes on squalane, acetyl tributyl citrate, and 1,2,3-tris(β-cyanethoxy)propane.[33–36]

The relationship between the chromatographic retention and the number of carbon atoms in the molecule z, with allowance for alternation, can be described by the equation:[37]

$$\lg t'_{R_z} = a_t + b_t z + c_t z^2 + d_t z^3 + D_t \varphi_z. \qquad (1)$$

where t'_{R_z} is the reduced retention time of the member of the homologous series with z carbon atoms in the molecule; a_t, b_t, c_t, D_t are constants; and $\varphi = +1$ for even values of z, or -1 for odd values.

Since the effect of alternation is fairly fine, it can be detected by examining not the retention time but the ratio of the reduced retention times

$$\sigma_\Gamma = t'_{R_z}/t'_{R_{z-1}}$$

or the difference between the retention indices ΔI of neighbouring homologues. In the study of the change in the retention characteristics with change in z for substances belonging to different homologous series, it is necessary to examine the ratio of the reduced retention times or the difference between the retention indices of substances having the same number of carbon atoms in the molecule but belonging to different homologous series. The quantity σ_Γ is related to the difference between the molar free energies of volatilisation from the stationary phase $\delta(\Delta G^\circ)_z$ of two molecules with numbers of carbon atoms in the molecule z and $z-1$ by the equation

$$\delta(\Delta G^\circ)_z = RT \ln \sigma_\Gamma, \qquad (2)$$

where R is the universal gas constant, and T the absolute temperature of the column.

Thus the contribution of the parity of the number of carbon atoms to the retention can be expressed in energy units.

On the graph, the distance between lines corresponding to series of homologues with even and odd values of z is characterised by the alternation criterion A_z:[16,17,37]

$$A_z = \lg \sigma_{\Gamma_{z+1}} - \lg \sigma_{\Gamma_z} = \lg t'_{R_{z-1}} + \lg t'_{R_{z-1}} - 2\lg t'_{R_z}, \qquad (3)$$

where σ_{Γ_z} and $\sigma_{\Gamma_{z+1}}$ relate to homologues with numbers of carbon atoms z, $z-1$ and $z+1$, z respectively. The sign of A_z depends on the parity of z and changes on going to each subsequent homologue.

The influence of the parity of z on the retention of n-alkanes, 1-bromoalkanes, and 2-alkanones by a stationary phase of medium polarity, namely triethylene glycol dibutyrate, was revealed using a highly efficient capillary column.[37] The study was carried out at temperatures of 40 °C and 80 °C. The alternation effect increases in the order: n-alkanes < 1-bromo-alkanes < 2-alkanones. This is clearly demonstrated by the plot of $\sigma(\Delta G^\circ)_z = f(z)$. The clearly defined zigzag character of this relationship for the 2-alkanones disappears on going to the 1-bromoalkanes and then to the n-alkanes. The $\sigma(\Delta G^\circ)_z = f(z)$ relationship for the n-alkanes is given by an almost straight line. The data obtained also indicate that in this case the temperature effect is slight; the influence of temperature is shown only by a displacement of the points on the graph, and the form of the curve giving the dependence of the chromatographic retention characteristics on z remains unchanged. An interesting feature is that the value of $\sigma(\Delta G^\circ)_z$ for 1-bromoalkanes with even values of z is smaller than that for the odd compounds, that is the change in these quantities is the opposite of that for the n-alkanes. This effect can be attributed to the role of the bromine atom in position 1, which makes the hydrocarbon chain longer, that is the number of "chain-forming" atoms in the 1-bromoalkanes with z carbon atoms must be regarded as $z+1$.

Fig. 1 gives graphs showing the influence of the parity of the number of carbon atoms in the molecule on various properties of n-alkanes.[37] It can be seen from Fig. 1 that the general curvature of the dependence of the retention values on z is determined by the regularity of the change in the values of the saturated vapour pressure of the sorbates (curve *1*). The influence of the parity of z on the retention of n-alkanes (curves *2* and *3*) is revealed to a greater extent when polyethylene glycol 400 is used as the stationary phase than when triethylene glycol dibutyrate is used; this is a consequence of the more rigid molecular structure of the first of these stationary phases. The similarity between curves *3* and *4* proves the close relationship between the retention values and the molecular structure of the compounds being considered.

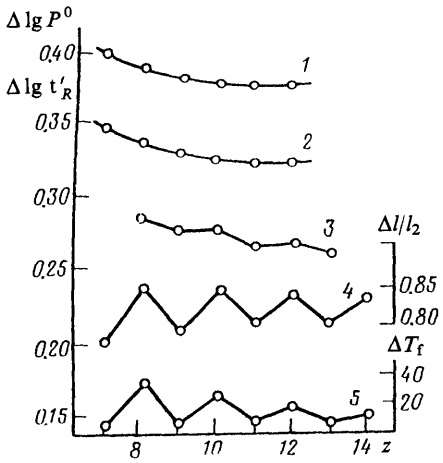


Figure 1. Dependence of various properties of n-alkanes on the number of carbon atoms in the molecule;[37] *1*, homologous difference between the logarithms of the saturated vapour pressures $\Delta \lg P^0$ at 80 °C; *2,3*, homologous difference between the logarithms of the reduced retention times at 80 °C on columns containing triethylene glycol dibutyrate (*2*) and polyethylene glycol 400 (*3*); *4*, the quantity $\Delta l/l_2$, where Δl is the difference between the terminal carbon atoms in the molecule for neighbouring homologues, and l_2 the length of the C–C bond; *5*, homologous difference between the melting points ΔT_f.

The influence of the parity of z on the functional group increment in the molecules of compounds of different homologous series has been studied.[38] The sorbates chosen were n-alkanes, bromoalkanes, aldehydes, and ketones. The study was carried out on a capillary column with triethylene glycol dibutyrate as stationary phase. The retention characteristic was the partial Henry coefficient (the capacity coefficient) $\Gamma' = t'_R/t_0$, where t_0 is the retention time of a substance which is not sorbed. The dependence of $\lg \Gamma'$ on z has the form of a broken line and can be described by an equation analogous to Eqn. (1).

Calculation of the retention increments from published data[39] shows that alternation of the values of ΔI is also observed for homologous series of methyl and chloromethyl esters of n-C_5–C_{12} chlorocarboxylic acids on capillary columns with the stationary phases SE-30 and Carbowax 20M.

The effect of alternation in the chromatographic retention of n-alkanes (C_6–C_{11}) is also observed on packed columns containing trifluoropropylmethylsilicone SKTFT-100 and pentaphenyl ether.[40] The $\sigma_\Gamma = f(t)$ relationship is given by a zigzag line. In particular, for the stationary phase SKTFT-100 the value of σ_Γ lies in the range 1.40–1.58 (uncertainty in the determination 0.01–0.04), and the quantity $\Delta\sigma_\Gamma = \sigma_{\Gamma_{z+1}} - \sigma_{\Gamma_z}$ characterising the range of alternation for following pairs of homologues has the values −0.11, 0.18, −0.14, 0.14.

The effect of alternation becomes particularly marked for polar sorbates and polar stationary phases. The alternation may be clearly defined even for packed columns with medium efficiency. In particular, this phenomenon has been studied in detail for aliphatic acids and their esters.[16,17,41] The regularities in the retention of the methyl esters of aliphatic acids were studied at different temperatures on four stationary phases with different polarity: Apiezon L, Triton X-305, Carbowax 20M, and diethylene glycol succinate (DEGS). The ratios of the retention indices of the sorbates studied on columns containing DEGS and Apiezon L showed a tendency to alternate. The alternation of these quantities is observed in the range $z = 3$–12, and the tendency disappears with further increase in the length of the alkyl group.

The retention of the dimethyl esters of aliphatic dicarboxylic acids on a column containing the high-temperature liquid-crystalline stationary phase bis(*p*-ethoxybenzylideneamino)biphenyl has been studied.[42] Clearly defined alternation of the retention values is observed for the C_4–C_8 series, after which it disappears with increase in the number of CH_2 groups in the molecule.

To investigate the alternation of the t'_{R_z} values, the alternation criterion A_z was calculated. The values of A_z were calculated for a temperature of 190 °C on two stationary phases: the polar DEGS and the non-polar Apiezon L. Alternation of the values of t'_{R_z} is observed only on the polar liquid phase in the range $z = 3$–6 for the dimethyl esters of dicarboxylic acids (t_0 = 190 °C, stationary phase DEGS); alternation of the retention characteristics is also observed in the range $z = 4$–10 for the free aliphatic acids (t_0 = 190 °C, stationary phase diethylene glycol adipate + H_3PO_4).

In the study of the chromatographic behaviour of free aliphatic acids it was shown that lowering the temperature of the column to 160 °C leads to disappearance of the alternation effect, and that the effect is preserved when the temperature is raised to 200 °C.

The alternation of the properties in the series of normal aliphatic acids is attributed to the difference between the configurations of the molecules of the even and odd homologues. In the monocarboxylic acids, the carboxyl group at one end of the molecule is opposite a methyl group for odd values of z) or a methylene group (for even values of z). For dicarboxylic acids, the carboxyl group is opposite a second carboxyl group or a methylene group, depending on whether the value of z is even or odd. Thus if the alternation is determined by the configuration of the molecule, it should be more clearly defined for the dicarboxylic acids and their derivatives. This is confirmed by the results obtained.[16,17] Thus if the range of alternation of the retention values is characterised by the difference

$$\Delta A_z = |A_{z+1}| - |A_z|,$$

then the range will be about 0.01–0.07 for free aliphatic acids, 0.06–0.08 for the methyl esters of aliphatic acids, and 0.16 for the dimethyl esters of dicarboxylic acids. The authors cited[16,17] consider that a definite role in the phenomenon of alternation may also be played by the polymorphism of the aliphatic acids (there exist forms

A, B, and C whose molecules differ in the magnitude of the angle at which the carbon atoms are arranged).

The effect of alternation has been observed[5] in the dependence of the relative retention of n-alkyl-substituted carboxylic acids (n-C_5 – n-C_{16}) on their melting points on a column containing a silicon + 15% stearic acid as stationary phase, the dependence of the relative retention of the methyl esters (n-C_8 – n-C_{18}) on the melting points of the corresponding aliphatic acids on a column containing a silicone grease as stationary phase, and the dependence on the melting points of the absolute specific retention volume of n-alkanols (C_1 – C_8) in a column containing the stationary phase SE-30.

A statistical estimation of the alternation effect has been carried out.[18] For this purpose, the uncertainty in the determination of the quantity used to characterise the chromatographic retention was established. This quantity was the retention increment ΔI equal to the difference between the retention indices I of neighbouring members of a series of sorbates differing in the number of repeating fragments. It was shown for a number of examples that the regularities of the change in the retention values in the series of sorbates studied are preserved when account is taken of the uncertainties in the determination of these quantities. Thus in the range of alternation $\Delta(\Delta I)$ for cycloalkanes on squalane in the range 3 – 13 I units, the uncertainty in the determination of I varies in the range 0 – 1.5 I units. Thus the alternation effect observed in a number of cases is not a consequence of the uncertainty in the determination of the retention indices, but is determined by the characteristics of the structure of the sorbates and the nature of their interaction with the stationary phase.

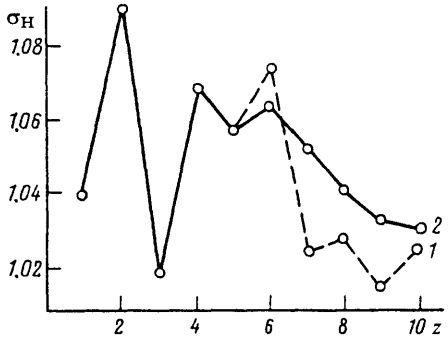


Figure 2. Dependence of the selectivity coefficient on the number of carbon atoms in the lateral alkoxy-group of symmetrical azoxy-ethers for smectic (*1*) and nematic (*2*) meso-phases.

The alternation effect is also revealed by the regularities of the chromatographic behaviour of liquid crystals when they are used both as sorbents and as stationary phases. For example, the alternation effect was detected in a chromatographic study of the thermodynamics of the solution of monohydric aliphatic alcohols in the cholesteryl ester of myristic acid.[43] The authors cited[43] consider that the probable reason for this effect is that when the molecules of non-mesogenic additives are introduced into the structure of a meso-phase there is a difference in the efficiency of the coupling between the molecules and individual sections of the meso-phase. The coupling reduces mainly to an end-type interaction between the molecules of the liquid crystal and the non-mesogenic additive. Increase in the length of the hydrocarbon group of the alcohol will lead to a decrease in the smectogenic character of the cholesteryl myristate molecules.

The selectivity of the stationary phases *p,p'*-methoxyethoxyazoxy-benzene (MEAB) with respect to isomeric alkanes (C_{10} – C_{17}) has been studied;[9,44] geometric isomers and positional isomers were examined. The dependence of the selectivity coefficient σ_H, which is the ratio of the reduced retention times of *trans*- and *cis*-isomers with double-bond position 2 – 8 or the ratio of the reduced retention times of neighbouring *cis*- and *cis*-isomers and *trans*- and *trans*-isomers, on the number z has a zigzag form. This confirms the influence of the parity of z on the ratio of the retention parameters of sorbates having the same number of carbon atoms in the molecule but belonging to different homologous series.

III. Even – odd effect in the retention of sorbates by homologous series of stationary phases

The effect of alternation in chromatography can also be detected by studying the retention of the same sorbates on a number of stationary phases which are members of one homologous series. In particular, this effect has been observed in a study of the separation of close-boiling isomers on columns containing nematic liquid crystals, namely azoxy-ethers. The influence of the parity of z can be examined from different viewpoints; thus it is possible to consider firstly the total number of carbon atoms in the molecule of the liquid crystal, and secondly the number of carbon atoms in both lateral parts; the influence of parity in one side chain on the chromatographic retention can also be examined. Thus symmetrical azoxy-ethers have been used as stationary phases for the separation of *m*- and *p*-xylenes.[45–47] The dimethoxy-derivative (azoxyanisole) has a low selectivity, the diethoxy-derivative (azoxyphenetole) a higher selectivity, and the subsequent homologues approximately the same or a lower selectivity (Fig. 2). If however the asymmetric ether *p,p'*-methoxyethoxyazoxybenzene is used as the stationary phase, the *m* – *p*-selectivity increases considerably and becomes greater than that for azoxyphenetole and its eutectic mixture with azoxyanisole.[48]

The change in the *m* – *p*-selectivity in a series of symmetrical and asymmetrical azoxy-ethers has been studied.[9,49] The value of the selectivity coefficient σ_H, which in this case is the ratio of the reduced retention times of the *m*- and *p*-xylenes, shows alternation not only with change in the number of carbon atoms in the side chains of the azoxy-compounds but also in the dependence on the symmetry of the molecules of the liquid crystals as a whole. The asymmetric azoxy-ethers on the whole have a greater *m* – *p*-selectivity than the symmetrical ones. In the series of asymmetric homologues, MEAB has the greatest *m* – *p*-selectivity.

An even – odd effect has been detected[50,51] in the retention of standard sorbates (ethanol, methyl ethyl ketone, benzene, and nitromethane) on liquid-crystalline stationary phases belonging to the homologous series of nitroazoxybenzenes. Alternation is shown by the values of the linear retention indices of the sorbates studied and the chromatographic polarity factors. The values of the retention parameters are greater for the odd than for the even substituents.

When asymmetric azoxy-ethers are used as stationary phases,[32] alternation is also shown by the values of the universal polarity factors — quantities which are proportional to the reduced retention times of the sorbates and which characterise the chromatographic polarity of the stationary phase with allowance for its sorptive capacity and the duration of the chromatographic analysis.

IV. Even–odd effect in liquid–liquid chromatography

The influence of the parity of z on the sorptive properties of petroleums is related to the corresponding regularities of their composition. Thus the ratio of odd and even n-alkanes in recent sediments and petroleums is different.[53–56] In sediments, molecules with an odd number of carbon atoms predominate, whereas in petroleums, molecules with an odd value of z are present in very small quantities or are not detected at all. It has been proposed[57] that this relationship be characterised by the odd-parity index, which is the ratio of the number of molecules of n-alkanes with odd values of z [odd molecules (O)] to the number of molecules of n-alkanes with even z [even molecules (E)]. The corresponding values of O/E are −5.6 in recent sediments, and 0.9–1.2 in petroleums.

The odd-parity index is used by many authors as a characteristic of petroleum which makes it possible to identify its origins. Another characteristic of petroleum used for identification is the ratio of the concentrations in it of two alkanes with an isoprene structure, namely pristane (2,6,10,14-tetramethylpentadecane) and phytane (2,6,10,14-tetramethylhexadecane).[58,59] For a long time, however, the predominance of even or odd alkanes (with normal or branched structures) in different petroleums was related in the literature only to the organic origin of the petroleum, and no account was taken of the fact that a change in its composition may take place during the migration of petroleum through rocks which are adsorbents. This was first pointed out by Vigdergauz and co-workers.[60] It is confirmed by the results of investigations[61,62] in which the effect of the alternation of the sorptive properties of n-alkanes was studied under liquid–liquid chromatographic conditions. When a mixture of n-alkanes is passed through a column containing silica gel moistened with hexane, a fraction richer in hydrocarbons of the even series will leave the column first, followed by a fraction richer in those of the odd series.

Fig. 3 shows the change in the ratios of the concentrations of neighbouring n-alkanes (containing z and $z-1$ carbon atoms in the molecules) in a comparison of the initial and final fractions of the eluate with the original mixture. The total coefficient of enrichment of the initial fraction of the eluate in n-alkanes of the even series was 1.24 for the chosen conditions.

Studies carried out with different adsorbents moistened with different organic substances gave initial fractions enriched sometimes in the even and sometimes in the odd homologues.

In the work cited,[62] the changes in the compositions of the petroleums were studied by gas–liquid and thin-layer chromatography. It was shown that the process of filtration of the petroleum through rock is accompanied by a change in the even : odd n-alkane ratio and in the pristane/phytane ratio compared with the ratios in the petroleum taken initially.

Finally, a detailed study has been made[63] of the effect of change in the composition of a mixture of hydrocarbons with the isoprene structure on filtration through moistened porous media. The work was carried out under the conditions of frontal liquid–liquid chromatography, which approach most closely the natural conditions of the migration of fluids. The porous medium used was activated silica gel moistened with n-hexane. The studies showed that an even–odd effect is also observed in this case. The concentration of pristane in the initial fractions increases, compared with the concentration of phytane. In subsequent fractions this sorption effect gradually decreases, and the composition of the filtrate approaches the original composition. The effect of change in the composition of the mixture of isoprene hydrocarbons under these conditions is determined both by the solubility of the hydrocarbons studied in the n-hexane wetting the adsorbent and by the adsorption surface of the polar activated silica gel used as the adsorbent.

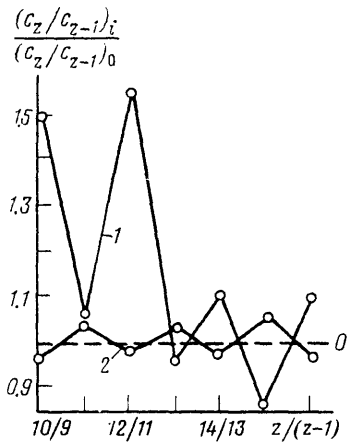


Figure 3. Change in the ratios of the concentrations of neighbouring n-alkanes (with numbers of carbon atoms in the molecules z and $z-1$) in a comparison of the initial (*1*) and final (*2*) fractions of the eluate with the original mixture (0).[60]

V. Other forms of alternation of retention values

A detailed examination of published data showed that the even–odd effect is only a particular case of alternation in chromatography. It is therefore of interest to examine the problem of alternation as a whole, and in particular the position occupied by the even–odd effect in alternation phenomena.

Study of the regularities of retention in different series of sorbates and stationary liquids makes it possible to consider seven cases of alternation of retention values.

1. With increase in the length of a molecule as a result of an increase in the number of repeating fragments (with a functional group on one or both ends of it). The even–odd effect, determined by the number of methylene groups in alkyl chains, is here a particular case.

2. On the successive addition of identical functional groups (or alkyl groups) to the repeating fragments of an aliphatic molecule or the aliphatic part of a molecule.

3. The analogous effect of a cyclic molecule (naphthenic or aromatic rings) and in per-substituted rings or heterocycles.

4. On displacement of a functional group (including hydrocarbon groups), joined to the alkyl chain of a molecule, along the chain.

5. The analogous effect for substituents in a cyclic molecule.

6. On the displacement of a functional group or a more complex fragment (or multiple bond), situated in a chain, along this chain (succession of metamers).

7. The analogous effect in heterocycles containing two heteroatoms.

Thus three types of alternation can be distinguished.

I. On the successive addition of identical fragments to a molecule (point 1).

II. On the successive addition of identical functional groups (or alkyl groups) to the fragments of an aliphatic chain or ring (points 2 and 3).

III. On the "displacement" of these fragments along alkyl chains and aromatic (or naphthenic) rings (points 4–7).

The initial data for the study of the relationships characterising the different types of alternation were the retention index values given in various sources,[64–69] and the published[45] and our own[10,70] values of the *m*–*p*-selectivity coefficients.

The retention characteristics used were the differences between the retention indices of neighbouring compounds in the series of sorbates selected

$$\sigma I = I_{N+1} - I_N,$$

where N is the sequence number of the compounds, and for the case of alternation in a series of liquid-crystalline stationary phases the selectivity coefficient σ_H, representing the ratio of the reduced retention times of *m*- and *p*-xylenes.

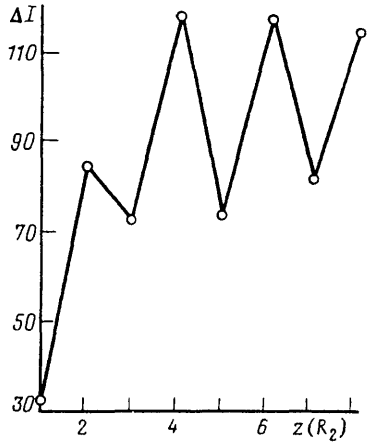


Figure 4. Dependence of ΔI on the number of carbon atoms in the substituent for n-alkyl acetates $CH_3-COO-C_zH_{2z+1}$ (z = 1–9) on a column containing OV-351.[64]

The graphical relationships which we obtained can illustrate the following classification of series of sorbates and stationary liquids in which alternation of the retention values takes place.

1. Series formed by an increase in the length of the aliphatic chain of a molecule as a result of an increase in the number of repeating fragments (structural units); the members of the series are homologues or polymer–homologues $R_1-\varphi-R_2$, where R_1 and R_2 are alkyl groups, and φ a functional group;

a, increase in length on one side of a functional group (or counting from a terminal methyl group); R_1 = const, $R_2 \neq$ const (Figs. 4–6);

b, increase in length in both directions away from a functional group; $R_1 \neq$ const, $R_2 \neq$ const; the side chains may increase in length to equal or different extents (Figs. 2 and 7).

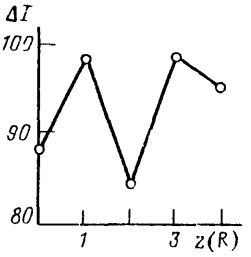
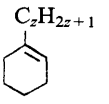


Figure 5. $\Delta I = f(z)$ relationship for n-alkyl derivatives of cyclohex-1-ene  (z = 1–5) on a column containing Apiezon L;[65] temperature of the experiment 100 °C.

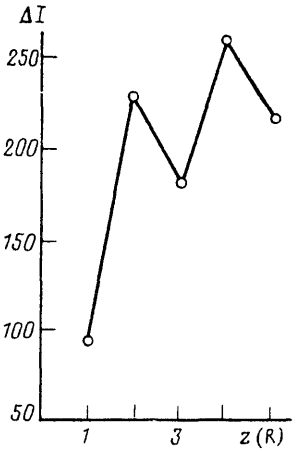
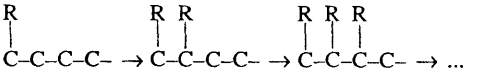
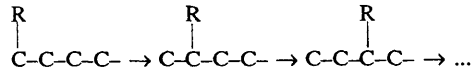


Figure 6. $\Delta I = f(z)$ relationship for di-n-alkylnitrosamines $(n\text{-}C_zH_{2z+1})_2N-NO$ (z = 1–6) on a column containing SE-30;[66] temperature of the experiment 125 °C.

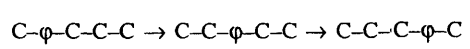
2. Series formed by the successive addition of identical functional groups (or alkyl groups) to the repeating fragments of an aliphatic molecule (or the aliphatic part of a molecule) or to a ring (formation of a polysubstituted chain or poly-substituted ring) (Figs. 8 and 9)



3. Series formed in the movement ("displacement") of functional groups or alkyl groups along a chain or ring (Fig. 10)



Series formed by "displacement" of insertion, that is a sequence of metamers



are included here.

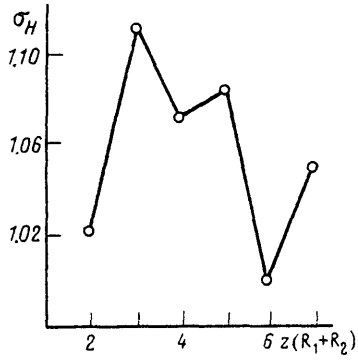
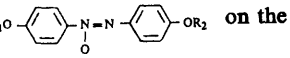


Figure 7. Dependence of the coefficient of $m-p$-selectivity σ_H of dialkoxyazoxybenzenes  on the total number of carbon atoms in both side chains of azoxy-ethers symmetrical and non-symmetrical structures.[10]

4. Obviously, alternation is also observed in isologous series, that is on going from saturated aliphatic hydrocarbons to alkenes and alkynes, and also from alicyclic to aromatic.

Studies have shown that the probability of the appearance of the alternation effect in chromatographic retention relationships is higher, the more polar the sorbates and stationary liquids studied. Thus in the study of retention on non-polar or slightly polar stationary phases (squalane, Apiezon L, SE-30, etc.), alternation is observed for such sorbates as alkyl-substituted cycloalkanes, aldehydes, ketones, and various esters, and is not observed for alkanes, alkenes, alkynes, or alkyl-substituted aromatic hydrocarbons. The range of alternation, defined as the difference between neighbouring values of ΔI in the selected series of sorbates, varies in the ranges 1–20 I units (sorbates—substituted cycloalkanes, aldehydes, ketones, esters of carboxylic acids; stationary phases—Apiezon L, SE-30, DS-550, OV-1), 1–50 I units (sorbates—substituted cycloalkanes, ketones, esters of carboxylic acids, alcohols, alkyl-substituted phospholans, substituted amines; stationary liquids—squalane, Apiezon L, SE-30, DS-550), and 1–100 I units (sorbates—substituted adamantanes, substituted amines; stationary phase—SE-30). On going to polar stationary phases, the effect of alternation becomes stronger and can also be observed for non-polar and weakly polar sorbates. For example, the range of alternation reaches 40 I units for such sorbates as alkylbenzenes, alkylamines, esters of carboxylic and benzoic acids, and alkyl-substituted cycloalkanes on columns containing PEG-4000, OV-351, XF-1150, dibutyl tetrachlorophthalate, and 1,2,3-tris(β-cyanethoxy)propane, 80 I units for alkyl-substituted cycloalkanes, cycloalkenes, and naphthalenes, esters of carboxylic acids, and alkylamines on columns containing PEG-1000, PEG-4000, PEGA, OV-351, and tricresyl phosphate, and 400–200 I units for alkylbenzenes, ketones, and esters of carboxylic acids on columns containing OV-351, XF-1150, tricresyl phosphate, and Reoplex.

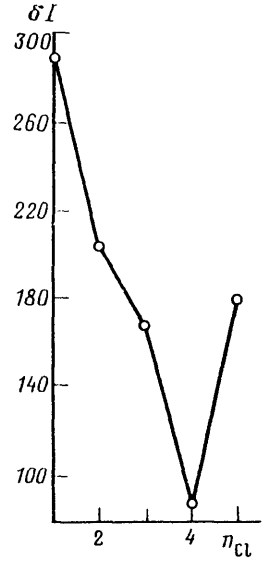


Figure 8. Dependence of δI on the number of chlorine atom for a series of chloro-derivatives of benzene: chlorobenzene, 1,2-dichlorobenzene, 1,2,3-trichlorobenzene, 1,2,3,4-tetrachlorobenzene, pentachlorobenzene, and hexachlorobenzene on a column containing Carbowax 20M.[67]

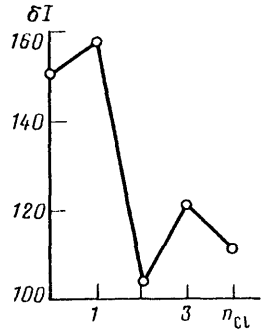


Figure 9. Dependence of δI on the number of chlorine atoms for a series of methyl esters of chloropropionic acids: $C_2H_5-COO-CH_3$, $CH_3-CHCl-COO-CH_3$, $CH_2Cl-CHCl-COO-CH_3$, $CH_2Cl-CCl_2-COO-CH_3$, $CHCl_2-CCl_2-COO-CH_3$, and $CCl_3-CCl_2-COO-CH_3$ on a column containing OV-101;[68] temperature of the experiment 80 °C.

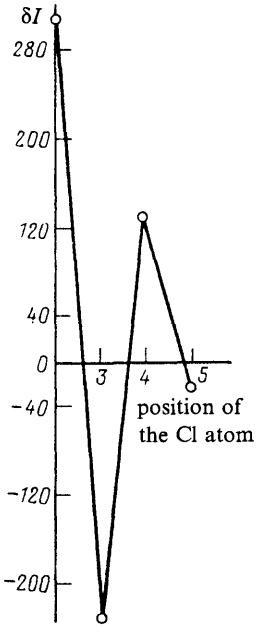


Figure 10. Dependence of δI on the position of the chlorine atom for a series of chlorinated salicylaldehydes on a column containing OV-351;[69] temperature of the experiment 140 °C.

It will be possible to determine more precise dependences of the retention values on the number of carbon atoms in the molecule and other physicochemical characteristics for identification, when more selective stationary phases appear. For a deeper understanding of the reasons for the production of the alternation effect it is necessary to study its relation to the structure of the molecules of the sorbates and stationary phases and the intermolecular interactions in the chromatographic column.

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Thus the effect of alternation of chromatographic characteristics is observed both in homologous series of sorbates and stationary phases (the even–odd effect) and in other series (for example on the "displacement" of a functional group along an aliphatic chain). The scale of the alternation for a sufficiently rigid molecular structure may reach 10–13 retention index units. The effect is detected in distribution and adsorption chromatography. Further studies may reveal this effect in other forms of chromatography (supercritical fluid, thin-layer, etc.). Different forms of alternation will possibly be detected.

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