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THE ROLE OF THE STATIONARY PHASE IN GAS-LIQUID CHROMATOGRAPHY AND METHODS OF SORBENT SELECTION

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The possibility of controlling the selectivity of the column is one of the principal advantages of chromatography (in the first place gas-liquid chromatography) over other methods for the separation of substances, the nature of the stationary phase constituting the main factor which determines the sequence of the elution of the components from the column and the relative elution times of the peak maxima [1-3]. Furthermore, the effect of the stationary phase extends also to the mode of spreading of the zones.

1. SELECTIVITY OF THE STATIONARY PHASE AND ITS RELATION TO THE DEGREE OF SEPARATION AND THE ERROR OF THE ANALYSIS

An investigator using gas chromatography is able to solve the following groups of problems: (a) qualitative analysis of the mixture; (b) quantitative analysis of the mixture; (c) isolation of a certain amount of pure substances or fractions; (d) determination of certain physicochemical characteristics of the test system.

In qualitative analysis the degree of separation must be sufficient to obtain in the chromatogram separate peak maxima of the individual components and the displacement of these maxima under the influence of the neighbouring components should be fairly small. In quantitative analysis it is important that the analytical error associated with the quality of the separation should be within the permissible limits.

In preparative chromatography the main requirement is to ensure the necessary purity of the fraction for a sufficiently large sample volume, which is also related to the degree of separation. Finally, in the determination of physicochemical characteristics the requirements are determined by the actual problem. Regardless of the aim of the chromatographic analysis, it is desirable that the separation should be attained in a short time.

The ratio of the distance between the ordinates of the maxima to the sum of the peak widths may serve as a measure of the separation of two components. Thus the degree of separation K is defined by the formula [1]:

$$K = \frac{\Delta l}{\mu_{0.5(1)} + \mu_{0.5(2)}},$$

where Δl is the distance between the ordinates of the maxima and $\mu_{0.5(1)}$ and $\mu_{0.5(2)}$ are the peak half-widths [1,4].
K can be found from the expression

$$K = \frac{V_{R_2} - V_{R_1}}{\omega_{0.5(1)} + \omega_{0.5(2)}} = 0.212 K_c \sqrt{n}, \quad (2)$$

where V_{R_1} and V_{R_2} are the retention volumes of the components, $\omega_{0.5(1)}$ and $\omega_{0.5(2)}$ the zone widths expressed in volume units, $K_c = 2(V_{R_2} - V_{R_1})/(V_{R_2} + V_{R_1})$ is the selectivity coefficient of the column, and $n = 5.55(V_R/\omega_{0.5})^2$ the number of theoretical plates characterising the efficiency of the column. The coefficient K_c depends not only on the nature of the stationary phase but also on the fraction of the column volume occupied by this phase. This follows from the equation

$$\frac{1}{K_c} = \frac{1}{k_c} + \frac{V_0}{V_{R_2} - V_{R_1}},$$

where $k_c = 2(V'_{R_2} - V'_{R_1})/(V'_{R_2} + V'_{R_1})$ is the selectivity coefficient of the stationary phase, V'_{R_1} and V'_{R_2} are the reduced retention volumes of the components, and V_0 is the gas volume (the retention volume of the non-sorbed substance).

Thus in order to achieve a satisfactory degree of separation of a two-component mixture, it is necessary that the zone spreading should be small and that the difference between the retention volumes, which is determined by the selectivity, should be large. By selectivity one should understand the property of the sorbent which gives rise to the relative displacement of the chromatographic peaks of the components.

The relation between the selectivity of the stationary phase and the degree of separation follows from Eqns. (2) and (3). However, K cannot be a complete characteristic of the conditions of analysis (determining whether or not they are satisfactory), since it does not determine unambiguously the magnitude of the analytical error (in quantitative analysis), the purity of the fraction (in the isolation of the components for preparative purposes), etc. Yet another important factor is the composition of the binary mixture to be separated. Furthermore, when the peaks are not separated completely, significant differences arise also in the calculation of K. Indeed, as a result of the mutual overlapping of the zones of neighbouring components, the peak width and sometimes also the value of Δl change (this has a particularly pronounced effect on the results of qualitative analysis) and therefore K determined from the general elution curve will differ from the value calculated from the individual curves for the components (the latter value will be called the effective separation factor K_{eff})[5]. It is frequently impossible to determine the peak width at the height necessary for the calculation of K.

Therefore, in order to estimate this degree of separation of overlapping peaks, it is desirable to employ the degree of separation defined by [5,6]

$$\psi = \frac{h_2 - h_{\min}}{h_2},$$

where h_2 is the height of the smaller peak and $h_{\min}$ the ordinate of the minimum between the peaks (Fig. 1). It has been shown[5-7] that the factor ψ, which varies steadily from 0 to 1 with K_{eff} and the ratio m of the heights of the neighbouring peaks, has important advantages over the previously employed factor $\theta = f/g$ (Fig. 1)[4,8,9], where f is the distance along the normal to the base line from the minimum to the point of intersection with the straight line joining the maxima and $g = f + h_{\min}$.

The relation between the degree of separation and the error of quantitative analysis (or the purity of the fraction in preparative chromatography) has been examined[5,10,11,12].

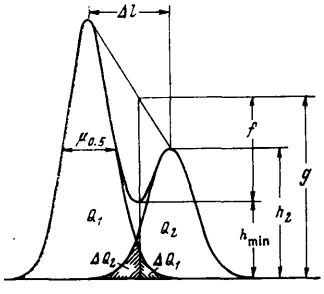


Fig. 1. Partial separation of peaks.

The column selectivity necessary to attain the required accuracy of the analysis (for specified column efficiency and peak ratio m) can be found from a nomogram[7].

Thus the selectivity of the stationary phase, which is the principal chromatographic characteristic of the latter, determines directly (other conditions being equal) the degree of separation and the error of the analysis of a two-component mixture.

2. INTERMOLECULAR INTERACTIONS IN THE COLUMN AND RETENTION CHARACTERISTICS

Raoult's law holds for an ideal dilute solution of a volatile substance:

$$p = xp^0, \tag{5}$$

where p^0 is the vapour pressure of the pure solute, p the vapour pressure of the solute over the solution, and x its mole fraction in the solution. In order to take into account positive and negative deviations from Raoult's law, the activity coefficient γ is introduced into the right-hand side of Eqn. (5). Then the combined Dalton–Raoult law can be represented by the formula

$$yP = \gamma xp^0, \tag{6}$$

where P is the total pressure in the system and y the mole fraction of the given substance in the gas phase.

According to Henry's law,

$$a = \Gamma c, \tag{7}$$

where a is the concentration of the solute in the liquid phase, c the concentration in the gas phase, and Γ Henry's constant; one can write

$$\Gamma = \frac{a}{c} = \frac{N_L + a}{N_G + c} \cdot \frac{x}{y} \simeq \frac{N_L}{N_G} \cdot \frac{x}{y}, \tag{8}$$

where N_L is the number of moles of the stationary liquid per unit volume of the liquid phase and N_G the number of moles of the carrier gas per unit volume of the gas phase. Since

$$P = N_G RT,$$

where R is the gas constant and T the absolute temperature, it follows from Eqns. (6)–(9) that

$$\Gamma = \frac{N_L RT}{\gamma p^0} = \frac{\rho RT}{\gamma p^0 M}, \tag{10}$$

where ρ and M are the density and molecular weight of the stationary liquid.

Thus the following expression can be obtained from Eqn. (10) for the specific retention volume V_g^T at a temperature T:

$$V_g^T = \frac{\Gamma}{\rho} = \frac{RT}{\gamma p^0 M}. \tag{11}$$

The specific (absolute) retention volume V_g is

$$V_g = \frac{273\,R}{\gamma p^0 M}. \tag{11a}$$

Next we establish the relation between Henry's constant and the principal thermodynamic characteristics of the system. The equilibrium between the gas and the liquid presupposes the equality of the corresponding free energies, $F_G = F_L$, where

$$F_G = F_G^0 + RT \ln c \quad \text{and} \quad F_L = F_L^0 + RT \ln a \tag{12}$$

(F_G^0 and F_L^0 are the standard free energies in the gas and liquid phases corresponding to a concentration of one mole per unit volume)†. Hence we have [14] the following equation:

$$\Delta F^0 = RT \ln \Gamma \tag{13}$$

or

$$\Gamma = e^{\Delta F^0/RT} = e^{-\Delta S^0/R}\, e^{\Delta H^0/RT} = \Gamma_S\, \Gamma_H, \tag{14}$$

where ΔS^0 is the entropy change per mole of substance on transition from the gas to the liquid phase and ΔH^0 the corresponding enthalpy change.

It follows from Eqn. (14) that the heat of solution Q, numerically equal to ΔH^0, can be determined from the following equation:

$$\frac{d \ln \Gamma}{d(1/T)} = \frac{\Delta H^0}{R}, \tag{15}$$

using a $\lg \Gamma$ (or $\lg V_R'$, $\lg V_N$, or $\lg V_g$)[4] plot. Evidently the following equation holds for the relative retention volume V^{rel}:

$$\frac{d \ln V^{rel.}}{d(1/T)} = \frac{\Delta Q}{R}, \tag{16}$$

where ΔQ is the difference between the heats of sorption of the component being analysed and a standard. If the enthalpy change is determined on the basis of the relation between the logarithm of the specific retention volume and the reciprocal of the absolute temperature [$d \ln V_g/d(1/T) = \Delta H'/R$], the following equation can be obtained [15,16]:

$$\Delta H' = \Delta H^0 + RT - \frac{RT^2}{\rho}\frac{d\rho}{dT} = 2{,}303R\, b \left(\frac{T}{T+C}\right)^2 + R\, T \left(1 - \frac{\beta T}{\rho}\right), \tag{17}$$

where b is the slope of the plot of $\lg \Gamma$ against $1/(T + C)$, C a constant, ρ the density of the stationary phase (g ml^{-1}), and β the constant in the relation $\rho = \alpha - \beta T$.

The contribution which the activity coefficient makes to the thermodynamic characteristics can be estimated for Eqns. (10) and (13). It has been shown [16-18] that

$$\frac{d \ln V_g}{dT} = -\frac{d \ln \gamma}{dT} - \frac{d \ln p^0}{dT} = -\frac{\lambda - \Delta h}{RT^2}$$

and

$$\frac{d \ln V_g}{d(1/T)} = \frac{\lambda - \Delta h}{R} = \frac{\Delta H'}{R}, \tag{18}$$

where λ is the latent heat of evaporation and Δh the excess enthalpy of solution (numerically equal to the heat of mixing) due to the deviation of γ from unity.

Adlard [19] showed that in the determination of the activity coefficient at infinite dilution γ^∞ from chromatographic data account must be taken of the non-ideality of the gas phase (by the method of Ashworth and Everett):

$$\lg \gamma^\infty = \lg \gamma + \frac{(B - v)(P - p^0)}{2.303\, RT}, \tag{19}$$

where B is the second virial coefficient in the equation of state of the gas and v the molar volume of the liquid solute.

By analogy with the derivation of Eqns. (13) and (14), one can write:

$$\lg \gamma^\infty = \frac{\Delta h}{RT} - \frac{\Delta s}{R}, \tag{20}$$

where Δs is the excess entropy of solution [17] and

$$\Delta h = R \frac{d \ln \gamma^\infty}{d(1/T)}. \tag{21}$$

The activity coefficient and hence the thermodynamic potentials are determined by the sum of the attraction and repulsion forces acting between the molecules in the chromatographic column. The total energy of the interaction of molecules in the liquid phase [1,14,20-23] consists of the energy of dispersion, induction, and orientation forces, the energy of specific interaction, and also the work expended to pull apart the solvent molecules‡.

As a result of the low concentration of the solute, the interaction between its molecules is usually disregarded although it has been shown in some studies [25] that in a number of cases the concentration effect does influence the results of the chromatographic process. Dispersion forces are of decisive importance in the interaction between the molecules of a non-polar solvent and a non-polar solute. They are due to the presence of virtual dipoles which give rise to an electric field inducing dipole moments in other molecules. Orientation forces arise between molecules with permanent dipoles due to their tendency to attain the orientation with the lowest energy. For example, orientation interaction occurs between sulphides and tricresyl phosphate molecules.

Induction forces act between the permanent dipole of one substance and the induced dipole of another. In particular, dipoles are induced in unsaturated and aromatic hydrocarbons. Although the energy of induction interaction is low, amounting to only 5–10% of the energy of dispersion interaction, it can nevertheless be sufficient to ensure the required chromatographic separation.

Specific forces include the hydrogen bond formed between a hydrogen atom and fluorine, oxygen, nitrogen, or chlorine atoms, donor–acceptor interaction, and complex formation.

The overall energy of interaction E between solvent and solute molecules can be represented by the following relation [22] when account is taken of dispersion, orientation, and induction forces:

$$E = -\frac{1}{r^6}\left(\frac{2}{3}\frac{\mu_1^2\mu_2^2}{kT} + \mu_1^2\alpha_2 + \mu_2^2\alpha_1 + 3\pi h \alpha_1\alpha_2 \frac{\nu_1\nu_2}{\nu_1 + \nu_2}\right), \tag{22}$$

where r is the distance between the molecules, μ_1 and μ_2 are the dipole moments, k is the Boltzmann constant, α_1 and α_2 are the polarisabilities of the solvent and solute molecules, h is the Planck constant, and ν_1 and ν_2 are the frequencies. The first term on the right-hand side of the equation characterises the orientation forces, the second and third terms the induction forces, and the fourth term the dispersion forces.

In his analysis of aliphatic acid esters on a column with an Apiezon grease, James [26] found that the dispersion forces decrease with increase in the branching and decrease of the molecular weight of the substances to be separated, because the esters of branched and unsaturated acids move in the column at a higher rate than those of saturated acids. It was shown that the dispersion forces are also influenced by the position of the double bond and the configuration of the molecule, in particular *trans*-isomers have somewhat higher retention volumes than *cis*-isomers

† The questions involved in the selection of the standard state have been examined in detail by James et al. [13]

‡ Kovats and Weiss [24] determined the contribution of these terms on the basis of retention indices [see Eqn. (46)].

and can be separated from the former when the efficiency of the column is equivalent to 4000 theoretical plates.

An example of the effect of induction forces is provided by separation using poly(ethylene glycol) and poly(propylene glycol) adipates as the stationary phases, described in James's paper quoted above. These liquids polarise the double bonds of unsaturated acid esters and increase the retention volumes of the latter, the positions of the double bonds and stereoisomerism being unimportant.

A very interesting example of the separation of components under the influence of induction forces is the chromatographic analysis of a mixture of thiophen and diethyl sulphide, using tricresyl phosphate as the stationary phase[27]. The boiling point and the dipole moment of diethyl sulphide are larger than those of thiophen, but, as a result of the high polarisation of thiophen which has aromatic properties, the latter is eluted after diethyl sulphide (here, as in the preceding example, donor–acceptor interaction evidently also takes place). On a column with a non-polar phase the components are of course eluted in the reverse order.

Hydrogen bonds are formed, in particular, between water and glycerol molecules, which permits the use of glycerol for the analysis of mixtures containing water[28]. When polyethylene oxide is used in the presence of amines, primary amines are strongly retarded and secondary amines less so. Tertiary amines have the smallest retention volumes due to the absence of the hydrogen bond with the stationary phase[29]. Evidently the role of the hydrogen bond in the overall energy of interaction between substances decreases with their molecular weight. Therefore the use of diglycerol or a polyester resin[21,30] as the stationary liquid in the analysis of alcohols makes it possible to elute ethanol first and methanol second.

Chromatographic separation can be achieved also with the aid of stationary phases which form complexes of varying stabilities with the components to be separated. Thus solutions of silver nitrate are widely used in the analysis of unsaturated hydrocarbons[31–35] and salts of aliphatic acids in the separation of amines[29]. The chromatogram obtained in the separation of gases on a column with a solution of silver nitrate in glycol shows that saturated hydrocarbons are eluted as a single peak, which is followed by the elution of the unsaturated compounds.

A novel method for the analysis of light gases has been described by Zhukhovitskii et al.,[36] who used blood as the stationary liquid for the selective retention of oxygen.

The theory of gas chromatography on columns with complex-forming phases (using silver nitrate solutions as an example) has been examined by a number of investigators[33,34]. In particular, Genkin showed[33] that Henry's constant can be determined from the equation

$$\Gamma = \Gamma^0 + \varkappa\Gamma^0 \; c_b \; , \qquad (23)$$

where $\varkappa = c_{ab}/c_a c_b$ is the stability constant of the complex, Γ^0 Henry's constant for the solvent containing the complex-forming agent, c_b the concentration of the complex-forming agent, and c_{ab} the concentration of the complex.

The work expended to pull apart the solvent molecules merits special examination. It has been shown[14] that, when a number of simplifying assumptions are made, this work A can be defined thus:

$$A = 4\pi r^2 \qquad (24)$$

where r is the radius of the solute molecule and σ the surface tension of the solvent. A increases with the size of the molecule in experiments with polar stationary phases and also with the polarity of the phases. Since A and E vary in the opposite sense, it has been concluded[37] that in the dissolution of non-polar substances the total interaction energy E decreases with increasing polarity of the solvent due to an increase of the work A; on the other hand, when polar substances are dissolved, the total energy increases with the polarity of the solvent. In this connection it is evident that for certain weakly polar substances the above effects can cancel out, resulting in an invariant Henry's constant (in the work quoted ethyl ether served as an example of such a weakly polar substance).

The role of the work A has been investigated in detail by Burrows and Preece[15]. If ΔE_A is the energy required to remove (at a constant temperature) the solute molecules from "holes" in the solvent and ΔE_C the energy liberated when the "holes" are filled up by solvent molecules (consequently ΔE_C is the energy of formation of the "holes"), the heat of sorption can be determined from the relation

$$\Delta H' = \Delta E_A - \Delta E_C + RT \; , \qquad (25)$$

where the last term characterises the excess work which must be performed.

The following expression holds for ΔE_A:

$$\Delta E_A = \frac{N(\epsilon_b - \epsilon_i)}{J} \; , \qquad (26)$$

where N is the Avogadro number, $\epsilon_b = \frac{1}{2}mv^2 \simeq \frac{1}{2}m(2\pi\nu r)^2$ the vibration energy of the solute molecule (when its mass is m and velocity v), r the radius of the "hole", ϵ_i the internal potential energy of the solvent molecule, and J the mechanical equivalent of heat (erg cal^{-1}). The radius of the "hole" can be determined as a function of Henry's constant in the following form:

$$r = 5.66 \times 10^7 \Gamma \, (\Delta E_A/2T)^{1/2} \cdot \exp(-\Delta E_A/RT) \qquad (27)$$

and

$$\Delta E_C = \Delta E_A - (\Delta H' - RT) = 18.1 \, r^2 (n+1)\sigma \; , \qquad (28)$$

where σ is the surface tension and n the constant in the relation between σ and temperature T; $18.1 = \pi N/J$.

An empirical relation derived by Burrows and Preece[15] for dinonyl phthalate (at 80°C) is of the form

$$\lg \Gamma = 0.62 \, \Delta E_A - 7.93 \; ,$$

where ΔE_A is expressed in kcal mole^{-1}. The radius of the "hole" was found to be about 3.4 Å.

The effect of the entropy factor on the chromatographic process has been investigated in a number of studies[15,17,37,38]. It has been shown that very often the separation of the sample components is in fact due to the differences in their entropies of solution. Korol'[38] obtained the following formula for the determination of the excess entropy of solution Δs:

$$\Delta s = \beta C_1 \ln \frac{1}{M} + C_2 \; , \qquad (30)$$

where β is a function of the heat of solution and the rigidity of the solvent and solute molecules ($\beta = 0$ corresponds to complete filling of the "holes" while maintaining the structure of the stationary phase), M the number of "holes" per mole of substance, and C_1 and C_2 are constants. Zhukhovitskii et al.[36] also examined the components of the excess entropies: the entropy of migration of the centre of mass

of the molecule and the entropy of rotation of the molecule and its individual parts, the first term being calculated from the excess entropy of a non-polar spherical molecule (carbon tetrachloride) in solution in a saturated hydrocarbon.

In concluding this section, the possibility of rapid chromatographic separation of high-boiling polar compounds may be pointed out. Since the low vapour pressure of such substances in the pure state is due to molecular association, the retention time is sharply reduced in chromatographic analysis on a column with a non-polar phase, where the interactions between solute molecules may be neglected and only dispersion forces act between solvent and solute molecules[5,38]. For example, in experiments on a column with n-heptadecane (at 22°C) the peak of ethylene glycol, which has a boiling point of 197.2°C, is recorded between the peaks due to hexane and heptane, which boil at 68.7° and 98.4°C respectively. Here of course particular attention must be paid to the selection of a carrier with low adsorption activity§. This procedure is also used in the analysis of polar substances by gas-adsorption chromatography[39].

Finally yet another peculiarity, which occurs in the analysis of polar substances on columns with polar stationary phases, may be noted. It has been shown[40-42] that here the absorption of the components being separated is accompanied by their adsorption on the surface of the liquid. Here the retention volume should be defined as the sum of two terms, one of which is the function of Henry's absorption constant and depends on the amount of the liquid phase and the other is a function of the surface excess Γ and depends on the area.

3. RELATION BETWEEN MOLECULAR STRUCTURE AND SORPTION PROPERTIES

One of the first attempts to establish the relation between the activity coefficient and the structure of solvent and solute molecules was made by Pierotti et al.,[43] who proposed the so-called "structural block" method. According to their concept, in which the interactions between the functional groups and alkyl radicals of both molecules are considered, the following relation should hold:

$$\lg\gamma = A + \frac{B - n_C}{n'_C} + \frac{C}{n_C + C'} + D\,(n_C - n'_C)^2 + \frac{F}{n'_C + F'} \quad , \qquad (31)$$

where n_C is the number of methyl and methylene groups in the solute molecule, n'_C the number of the corresponding groups in the solvent molecule, and A, B, C, D, F, C', and F' are constants[20]. A linear relation between $\lg\gamma$ and the number of carbon atoms in the solute molecule follows from Eqn. (31) for the analysis of homologues on a column with a definite phase. In the choice of stationary phases and also in the identification of the components of the mixtures being analysed, relations between retention volumes and the number of carbon atoms in the molecule, the boiling point T_b, or the vapour pressure p^0, which are valid within the limits of a single homologous series of solutes, are widely used. Herington[44] showed that, for the logarithm of the retention volume defined by

$$\lg V^{rel} = \lg\frac{p_1^0}{p_2^0} + \lg\frac{\gamma_1}{\gamma_2} \quad , \qquad (32)$$

where subscript 1 refers to the component being analysed and subscript 2 to a standard, the following relations hold,

$$\begin{aligned} \lg V^{rel} &= a + b\ n_C, \\ \lg V^{rel} &= a_T + b_T\ T_b \quad , \\ \lg V^{rel} &= a_s - b_s \lg p^0 \quad , \end{aligned} \qquad (33)$$

where a, b, a_T, a_s, and b_s are constants whose values depend on the nature of the stationary phase, the working temperature, and the homologous series of the substances being separated.

There is a linear relation also between the retention volumes of the components of a given homologous series on two columns with different stationary phases[45]. Fig. 2 shows that in separation on a column with a non-polar phase the straight lines corresponding to different homologous series are significantly closer to one another than in separation on a polar phase[46].

The selectivity coefficient k'_s for adjacent components of the same homologous series is of course constant, since the heat of solution Q is an additive quantity:

$$Q = Q_0 + Q_{CH_2}\ n_C \quad , \qquad (34)$$

where Q_0 and Q_{CH_2} are constants.

Zhukhovitskii and coworkers[1,47] proposed a more general relation than Eqn. (33):

$$\lg V^{rel} = a' + b'\frac{T_b}{T} \quad , \qquad (35)$$

which holds over a definite range of working temperatures T. Relations between the retention volumes and other physicochemical characteristics of the substances to be separated,

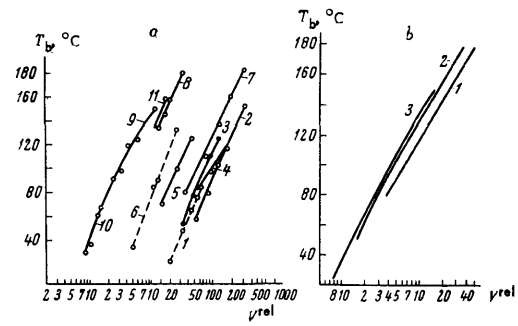


Fig. 2. Variation of the relative retention volumes with the boiling points[44]:
a) column with di(β-cyanoethyl) ether; temperature 67°C: 1) aldehydes; 2) ketones; 3) acetates and formates; 4) alcohols; 5) acetylenes; 6) ethers; 7) alkylbenzenes; 8) alkylcyclohexanes; 9) straight-chain saturated hydrocarbons; 10) olefine; 11) alkylcyclopentanes;
b) column with Fluorolube; temperature 100°C: 1) alkylbenzenes; 2) cycloalkanes; 3) straight-chain saturated hydrocarbons, methylparaffins, and olefins.

§ Without considering in detail the questions associated with the choice of the solid carrier, it may be noted that the interfering effect of the latter on the retention characteristic is often very considerable.

for example refraction[48], the parachor[49], dipole moment[50], etc., are also used in practice. Anvaer et al.[14] showed that, when the work expended to remove equal volumes of the solvent and solute (saturated hydrocarbons) is the same the heat of solution Q should be related to the heat of evaporation λ_v as follows:

$$Q = \frac{\lambda_v}{V_1} V_2 \ , \qquad (36)$$

where V_1 and V_2 are the molar volumes of the solvent and solute. Consequently a linear relation between the logarithm of the reduced retention characteristic and V_2 should hold within the limits of each homologous series.

A method for the calculation of retention parameters, based on the physicochemical characteristics of the solvent and solute, has been proposed by Martire[51], who started with Hildebrand's equation:

$$\ln \gamma = \frac{V_2}{R \cdot T} \Phi_1^2 (\delta_1 - \delta_2)^2 \ , \qquad (37)$$

where V is the molar volume, Φ_1 the volume fraction of the solvent in the solution, $\delta = \sqrt{\lambda_v / V}$ is a solubility parameter, subscript 1 refers to the solvent and subscript 2 to the solute. Since Eqn. (37) holds only for non-polar molecules and for positive deviations from Raoult's law, Martire added appropriate terms and obtained the relation

$$\ln \gamma = \frac{V_2}{R \cdot T} \Phi_1^2 [(\delta_1 - \delta_2)^2 + (\omega_1 - \omega_2)^2 - C] \ , \qquad (38)$$

where $\omega \simeq \mu^2/V$, μ is the dipole moment, and C characterises the negative deviation from Raoult's law, $C = k(V_2/\delta_2)$ and k depending only on the nature of the solvent.

Anvaer[52] based his treatment on a familiar model, according to which the transfer of a molecule with radius r and dipole moment μ from the vacuum into a dielectric with dielectric constant ϵ involves an energy gain:

$$\Delta E = \frac{2}{9} \frac{\mu^2}{r^3} \left(1 - \frac{1}{\varepsilon}\right) \ . \qquad (39)$$

If it is assumed that the work ΔE corresponds to the free energy change, there is a linear relation between the logarithm of Henry's constant (or the logarithm of the relative retention volume) of any component and $1/\epsilon$. This hypothesis has been used[52] to classify stationary phases.

It is interesting to examine the variation of sorption characteristics within a homologous series of stationary liquids. According to the Clausius–Mosotti equation, the molecular polarisation P_{mol} is

$$P_{mol} = \frac{\varepsilon - 1}{\varepsilon + 2} V_1 = \frac{4}{3} \pi N \left(\alpha + \frac{\mu^2}{3kT}\right) \ , \qquad (40)$$

where $\alpha = \alpha_{at} + \alpha_{el}$, α_{at} is the atomic polarisability, α_{el} the electronic polarisability, $\alpha_{or} = \mu^2/3kT$ the orientation polarisability, and k is the Boltzmann constant. Using the equation $\frac{4}{3}\pi N \alpha_{el} = M_R$, where M_R is the molecular refraction, Sakharov[53] obtained the relation

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{M_R}{V_1} + \frac{4}{9} \frac{\pi N}{kT} \frac{\mu^2}{V_1} \ . \qquad (41)$$

The ratio M_R/V_1 and the dipole moment are almost constant within a homologous series and therefore, in accordance with Onsager's equation, we have

$$\Delta E = \frac{\mu^2}{r^3} \frac{\varepsilon - 1}{2\varepsilon + 1} \ , \qquad (42)$$

which is more accurate than Eqn. (39), since the mutual polarisation of molecules is taken into account. Sakharov

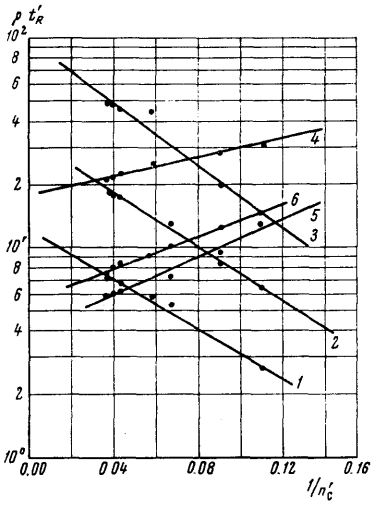


Fig. 3. Variation of the product of the reduced retention time t'_R and the density of the stationary phase ρ with the reciprocal of the number of carbon atoms in the molecule of the stationary phase (dialkyl phthalates); temperature 50°C:
1) n-hexane; 2) n-heptane; 3) n-octane; 4) benzene; 5) methanol; 6) ethanol.

showed that the following equation holds for a particular component:

$$\lg \Gamma \simeq A \frac{1}{V_1} + B \ . \qquad (43)$$

Indeed it has been shown in the work of Chovin and Ducros[54], Petsev and Dimitrov[55], and the author of the present review[56,57] that the relation between $\lg \Gamma$ and the number of carbon atoms n'_C in the stationary phase molecule is nonlinear, although it does approach linearity for fairly high values of n'_C. However, the plot in Fig. 3 shows that the relation between $\lg \Gamma$ and $1/n'_C$ is in fact linear.

4. CLASSIFICATION OF STATIONARY PHASES

A number of investigators have based the classification of stationary phases on the relation between the polarity and the retention characteristics of specified substances. Rohrschneider[58] placed the stationary phases along the abscissa axis (Fig. 4) so as to obtain a linear variation of the logarithm of the retention volume of divinyl relative to butane on transition from one phase to another. A polarity of zero was attributed to squalane and a polarity of 100 to di(β-cyanoethyl) ether. This made it possible to characterise stationary phases by the corresponding polarity indices.

In other investigations[59–62] almost the same method of classification was used but with the difference that acetylene and ethane, methanol and butane, two straight-chain saturated hydrocarbons, etc. were used as standards. Sakharov[53,63] showed that all these methods follow from the general relation

$$\lg V^{rel} = B_1 \lg V_{st}^{rel} + B_2 \ , \qquad (44)$$

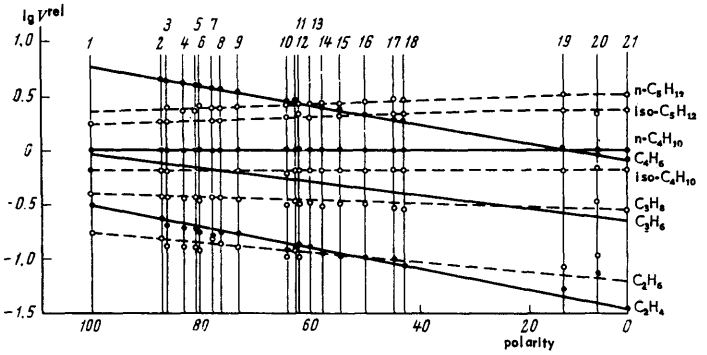


Fig. 4. Relation between the retention volume of a substance (relative to n-butane) and the polarity of the stationary phase[53]:
1) di(β-cyanoethyl) ether; 2) *N*-methylacetyl-β-aminopropionitrile; 3) *N*-formylmorpholine; 4) propylene glycol carbonate; 5) ethyl cyanoacetate; 6) dimethylformamide; 7) poly(ethylene glycol) 600; 8) glycol sulphite; 9) acetonylacetone; 10) benzyl cyanide; 11) diethylformamide; 12) diethylcyanamide; 13) propylene glycol sulphite; 14) epoxypropylmorpholine; 15) 1,3-butylene glycol sulphite; 16) *N*-β-hydroxypropylmorpholine; 17) dibenzyl ether; 18) dibutylformamide; 19) 1-chlorooctadecane; 20) silicone oil; 21) squalane.

where V^{rel} is the relative retention volume of a particular component, V_{st}^{rel} the relative retention volume of the standard, and B_1 and B_2 are constants; B_1 characterises the polarity of the substance being analysed and lg V_{st}^{rel} serves as the characteristic of the polarity of the solvent (for the latter one can use not only the logarithm of the retention volume of the standard but also some other suitable quantity in particular $1/\epsilon$). Sakharov pointed out that the correct choice of the standard can significantly reduce the error in the determination of retention characteristics; it is recommended that a substance belonging to the same class of compounds as the component being analysed should be selected as the standard.

The above method of classification has important advantages because it greatly simplifies the choice of stationary liquids for the separation of particular mixtures and also for the identification of unknown components. However, it also has a number of disadvantages, associated with failure to take into account the entire wide variety of intermolecular interactions between stationary phases and the substances being separated.

Plots of the retention index [see Eqn. (46)] against the polarity of the stationary phase have been quoted by Chovin[54]. Lazarse and Roumazielles[65] showed that the relation between the polarity and the ratio of the reduced retention volumes of straight-chain saturated hydrocarbons (with $z + 1$ and z carbon atoms in the molecules) multiplied by the absolute temperature of the column is of the same type.

The method proposed by Brown[66] is based on a characteristic of only the donor–acceptor properties of stationary phases. On a triangular graph, each phase has a point with the coordinates

$$\frac{V_n}{V_n+V_a+V_d}, \frac{V_a}{V_n+V_a+V_d}, \text{and} \frac{V_d}{V_n+V_a+V_d},$$

where V_n, V_a, and V_d are respectively the retention volumes of a non-polar substance and an electron acceptor and donor on a column with the given phase. n-Hexane, ethanol, and 2-butanone and also n-decane, 1,1,2-trichloroethylene, and dioxan have been used as the standard substances for the determination of the properties of the phases. The position of the point relative to the vertices of the triangle can serve as a characteristic of the phase.

5. METHODS OF SELECTION OF STATIONARY PHASES

In selecting the stationary phase to solve a particular analytical problem the greatest attention is of course given to the selectivity of the phase. Furthermore, there are additional requirements, which include: (1) the absence of chemical interaction with the substance to be separated, the solid carrier, the column wall, and the carrier gas; (2) chemical stability under operating conditions; (3) low vapour pressure under operating conditions; (4) low viscosity. It is desirable that the phase should be readily available and that it should contain the minimum amount of impurities.

Depending on the composition of the mixture to be analysed, the following aspects of selectivity should be considered; (1) selectivity as the capacity to separate any two components; (2) selectivity as the capacity to separate the components of a single homologous series; (3) selectivity as the capacity to separate the components of two (or several) homologous series[67].

The selection of the stationary phase for the separation of two components must be based in the general case on the retention characteristics of the substances taken from the literature[1,9,68–74] or determined experimentally. In the analysis of homologues the principal criterion in the selection of the stationary phase is the coefficient b in the equa-

tion relating the logarithm of the reduced retention characteristic and the number of carbon atoms in the molecule [see Eqn. (33)]. For adjacent homologues, the selectivity coefficient k_s of the stationary phase is

$$k_s = 2\frac{10^b - 1}{10^b + 1} \quad (45)$$

i.e. the selectivity is greater the larger is b.

If instead of the retention volume one uses[75-78] as the retention characteristic the retention index I, defined by

$$I = r\frac{\lg V'_{R_x} - \lg V'_{R_z}}{\lg V'_{R_{(z+r)}} - \lg V'_{R_z}} + z \quad (46)$$

(a quantity larger by a factor of 100 was used by Kovats and coworkers[75-78]), where V'_{R_x}, V'_{R_z}, and $V'_{R_{z+r}}$ are the reduced retention volumes of the substance analysed and straight-chain saturated hydrocarbons with z and $z + r$ carbon atoms in the molecules, then the selectivity, considered as the capacity to separate homologues, can be estimated as the difference between the retention indices of adjacent homologues:

$$\Delta I = b/b_p \ , \quad (47)$$

where the coefficient b_p refers to the homologous series of straight-chain saturated hydrocarbons (paraffins).

If the problem is to separate the components of two homologous series, it is necessary to use a stationary phase which causes a shift of the $\lg V^{rel} - n_C$ linear plot for one series relative to that for another, and the shift can serve as a measure of the selectivity of the phase.

Bayer and Rock[79] introduced a selectivity factor δ, which is equal to the ratio of the reduced retention characteristics of two substances belonging to different homologous series and having different boiling points (or more precisely substances which have the same vapour pressures at the working temperature):

$$\delta = \frac{V'_{R_2}}{V'_{R_1}} = \frac{p_1^0\gamma_1}{p_2^0\gamma_2} = \frac{\gamma_1}{\gamma_2} \ . \quad (48)$$

The values of δ for various sorbents and classes of substances to be separated, determined by graphical interpolation, have been widely used[68,80].

It can be shown that the relation between the factor δ and the selectivity coefficient k_s is

$$k_s = 2\frac{10^b - 1}{10^b + 1} = 2\frac{\delta\left(\frac{p_1^0}{p_2^0}\right)^{b_s} - 1}{\delta\left(\frac{p_1^0}{p_2^0}\right)^{b_s} + 1} \quad (49)$$

when $\delta(p_1^0/p_2^0)^{b_s} > 1$, which corresponds to the elution of the components in the sequence 1–2, and

$$k_s = 2\frac{\frac{1}{\delta}\left(\frac{p_2^0}{p_1^0}\right)^{b_s} - 1}{\frac{1}{\delta}\left(\frac{p_2^0}{p_1^0}\right)^{b_s} + 1} \quad (50)$$

when $\delta(p_1^0/p_2^0)^{b_s} < 1$, which corresponds to the reverse sequence. Instead of $(p_2^0/p_1^0)^{b_s}$, one can use the expression $10^{b\Delta T_b}$, where ΔT_b is the difference between the boiling points of the components to be separated.

Thus the phase with the greatest or smallest factor δ (i.e. the phase which ensures the highest value of the coefficient k_s) is the most effective for the separation of a pair of substances belonging to different homologous series.

Suppose, for example that such pairs are heptane–hept-1-ene and decane–benzene. Fig. 5 shows the relation between the logarithms of the reduced retention volumes and the boiling points of straight-chain saturated hydrocarbons, straight-chain olefins, and alkylbenzenes in analysis on columns with squalane and adiponitrile[67]. It is evident from the graph that δ for olefins and saturated hydrocarbons is 1.90–1.95 on adiponitrile and 1.0 on squalane.

Adiponitrile is one of the most selective phases for the separation of the above classes of compounds. Calculation of the coefficient k_s shows that it is 0.15 for the non-polar phase and 0.53 for the polar phase and thus the latter is preferable. On the other hand, because of the considerable difference between the boiling points of benzene and decane, in their separation the non-polar phase with δ = 1.2 is preferable to the polar phase with δ = 16.0, since in the first case we have k_s = 1.8 and in the second 0.3.

It follows from the above example that the choice of the best phase for the separation of any pair of substances can be based on the tabulated values of δ.

Similarly it is possible to select optimum phases for the analysis of 3- and 4-component mixtures of substances belonging to two homologous series[67]. Thus if substances 1 and 2 belong to one series and substance 3 to another,

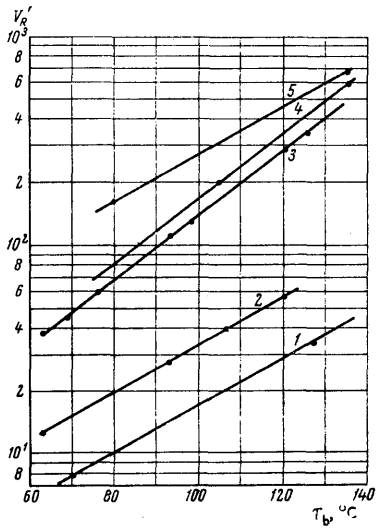


Fig. 5. Relation between the reduced retention volumes and the boiling points of hydrocarbons on columns with squalane and adiponitrile at 40°C:
1) straight-chain saturated hydrocarbons, adiponitrile; 2) straight-chain olefins, adiponitrile; 3) straight-chain saturated hydrocarbons and straight-chain olefins, squalane; 4) aromatic compounds, squalane; 5) aromatic compounds, adiponitrile.

the optimum value of δ for a phase which would ensure elution in the sequence 1–3–2 is

$$\delta = \frac{(p_3^0)^{b_s}}{(p_1^0\ p_2^0)^{0.5 b_s}} \quad \text{or}$$

$$\lg \delta = 0.5\, b_\tau (T_{b_1} + T_{b_2} - 2T_{b_3}) \qquad (51)$$

it being assumed that the values of b_s are similar for both series.

Since the order of elution is influenced both by the selectivity of the phase and the vapour pressures of the components, evidently by itself a certain degree of selectivity of the phase in relation to one of two homologous series does not ensure the separation of these components. Thus mixtures of straight-chain saturated hydrocarbons and alkylbenzenes have been separated on columns with technical fractions of aliphatic acids as the stationary phases[81]. The corresponding chromatograms are shown in Fig. 6. Whereas on the column with the light acid fraction the benzene peak is superimposed on the heptane peak, when the vat residue is used the retention volume of benzene increases and the latter is eluted after heptane. Even greater selectivity in relation to aromatic hydrocarbons is shown by the middle acid fraction on a column in which benzene is eluted together with octane.

Thus it is evident from the chromatograms that, although the middle acid fraction is in fact more selective, the vat residue or even the non-polar liquid paraffin are more suitable for a clear separation of saturated hydrocarbons and alkylbenzenes (Fig. 7).

In the separation of components belonging to two homologous series approximately equal separation factors for all pairs of peaks can be achieved in two ways[82]:

a. By using a selective sorbent characterised by

$$k_{s1,2} = \frac{10^{b_s(m+1)} - 1}{10^{b_s} - 1} k_{s1} \text{ and } k_{s1} \simeq k_{s2}\ , \qquad (52)$$

where $k_{s1,2}$ is the selectivity coefficient with respect to the lightest of the components to be separated in both series, m the difference between the numbers of carbon atoms in the molecules of the last and first component of the first homologous series, and k_{s1} and k_{s2} are the selectivity coefficients for adjacent components of the first and second homologous series. An example of such separation is the analysis of a mixture of straight-chain saturated hydrocarbons and alkylbenzenes on a column with di(β-cyanoethyl) sulphide, where benzene is eluted after nonane. The fraction width Δn, defined as the number of components of the first series which can be separated from the components of the second series, is $\Delta n = m + 1 = 4$. In the examples quoted above with aliphatic acid fractions as stationary phases (Fig. 6) $\Delta n = 1$ for the column with the light fraction and $\Delta n = 2$ for the column with the middle fraction.

b. By using a sorbent of moderate selectivity, characterised by

$$k_{s1,2} \simeq 0.5\, k_{s1} \text{ and } k_{s1} \simeq k_{s2}\ , \qquad (53)$$

i.e. a sorbent which ensures the alternation of the components of both series on elution.

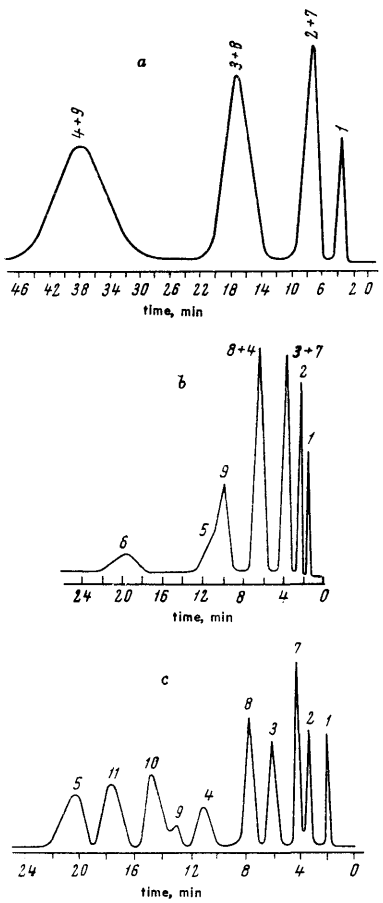


Fig. 6. Chromatograms of mixtures of straight-chain saturated hydrocarbons and alkylbenzenes on columns with different aliphatic acid fractions:
a) light fraction; *b*) middle fraction; *c*) vat residue;
1) hexane; 2) heptane; 3) octane; 4) nonane;
5) decane; 6) undecane; 7) benzene; 8) toluene;
9) ethylbenzene; 10) *m*- and *p*-xylenes; 11) *o*-xylene.

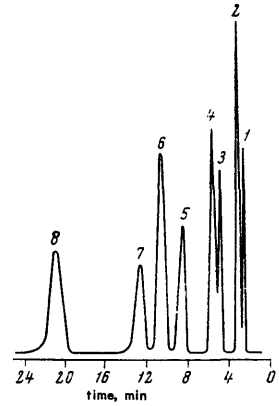


Fig. 7. Chromatogram of hydrocarbons on a column with liquid paraffin:
1) benzene; 2) heptane; 3) toluene; 4) octane;
5) ethylbenzene; 6) nonane; 7) isopropylbenzene; 8) decane.

Relations (53) can hold within wide limits only when the coefficients b_1 and b_2 are identical for both series. Therefore the maximum width of the fraction to be separated should be defined by the formula

$$\Delta n = m + 1 = \frac{0.5\, b_1}{b_2 - b_1} + 1 \quad . \tag{54}$$

The last condition corresponds to the relation $k_{s1,2} \geq 0.25\, k_{s1}$, i.e. the light component of one series is located midway between two components of the second series and is somewhat displaced towards one of them.

The choice of individual sorbents satisfying the specified conditions is very difficult in many cases, particularly when one deals with the separation not of two but of a large number of homologous series. The search for such sorbents to solve each concrete problem would result in an excessive number of phases used, which is already fairly large. Therefore considerable importance attaches to the use of binary sorbents permitting fine regulation of the selectivity and enabling the peaks on the chromatogram to be displaced relative to one another. A separate section deals with this question.

The procedure involved in the selection of the stationary phase can be significantly simplified by using the relation between the molecular structure of the substance to be separated and its absorption capacity. Recently a number of communications have appeared, dealing with the possibility of calculating the retention volumes assuming additivity, by adding together the increments corresponding to the functional groups[83-87] or different subtypes of the bonds between carbon atoms[88,89]. It is then assumed that

$$\lg V^{rel} = \Sigma n_{ij} A_{ij} \quad , \tag{55}$$

where n_{ij} is the number of bonds of the given subtype in the molecule of the substance being analysed (or functional groups of the given type) and A_{ij} is the corresponding increment. Eqn. (55) follows from the additivity of the free energy change[90,91], becoming more accurate when a constant term A_0 is introduced on the right-hand side. Special cases of Eqn. (55) are Eqn. (33) and also the method of calculation by the interpolation procedure proposed by Evans and Smith[92].

The authors who calculated retention volumes by the additive procedure used this method only for substances of one class. Indeed when many sorbents are used, the increment per CH_2 group (or bond between secondary carbon atoms) can vary from one homologous series to another. This follows, in particular, from the fact that the $\lg V^{rel}$–n_C lines are not parallel[20,93]. The corresponding lines for various classes of hydrocarbons and their derivatives are parallel only when non-polar solvents are used. Then the method of calculation of retention characteristics by this procedure becomes universal. Evidently the magnitude of the increment is an indication of the selectivity of the phase in relation to the components whose molecules contain the corresponding group or bond[94].

The retention index[75] has significant advantages as a retention characteristic, the additivity of the reduced characteristics entailing the additivity of the index:

$$I = \Sigma n_{ij} B_{ij} + B_0 \quad , \tag{56}$$

where B_{ij} is the increment per bond (or structural group) and B_0 is a constant.

One of the consequences of Eqn. (56) is the constancy, noted by Evans and Smith[95], within the limits of a homologous series, of the quantity $M_e - M = \Delta M_e$, where M is the molecular weight of the substance and M_e an effective molecular weight equal to the product of the retention index and the sum of the atomic weights of one carbon and two hydrogen atoms (14.026), and also the constancy of "the retention characteristics of the functional group" noted by Swoboda[96].

The difference between the retention indices of two components belonging to different homologous series but containing the same number of carbon atoms in their molecules is a characteristic whereby it is possible to estimate rapidly the suitability of a particular phase for the separation of concrete mixtures. This quantity (δI), which is the difference between the increments per group (or per bond subtype) in the molecules of the series to be separated, is readily tabulated, and does not require a correction for the vapour pressure, which is essential when the factor δ is used. When the coefficients b for homologous series are different, it is necessary to use either average values (as is done in the tabulation of δ values) or values of c and d from Eqn. (57) are tabulated:

$$\delta I = c + d n_C \quad . \tag{57}$$

The relation between δ and δI is given by equation[97]:

$$\lg \delta + b_T \Delta T_b = b\, \delta I$$

or

$$\lg \delta + b_s \lg \frac{p_1^0}{p_2^0} = b\, \delta I \quad , \tag{58}$$

where p_1^0 and p_2^0 are the vapour pressures of the substances to be separated, ΔT_b the difference between their boiling points, and b, b_T, and b_s are the coefficients of Eqn. (33).

The difference between the retention indices of a standard substance on squalane and the test phase has also been used as a characteristic of the polarity of the stationary phase[98]. Finally, Rohrschneider[99,100] suggested that the retention indices be calculated from the formula

$$I = I_0 + ax + by + cz + du + es \quad , \tag{59}$$

where I_0 is the retention index on a column with squalane, a, b, c, d, and e are characteristics of the substance being analysed, and x, y, z, and s are characteristics of the stationary phase.

So far the problem of the selection of stationary phases has been examined only from the standpoint of achieving a definite selectivity without taking into account additional limiting factors, for example the duration of analysis, the column length, the hydraulic resistance of the column[1] etc. It is desirable to select the optimum separation conditions: (a) for a specified accuracy of the analysis (degree of separation of the least readily separated pair of components) on a column of given length with the aim of achieving the fastest possible separation; (b) on a column of given length with the aim of achieving the highest degree of separation; (c) for a specified accuracy with the aim of achieving the most rapid analysis. Therefore, apart from selectivity, it is necessary to consider as the principal properties of the stationary phase its sorption capacity in relation to the most strongly sorbed component and the diffusion characteristics, which are determined by the viscosity.

If the problem is to select a sorbent to attain the most rapid analysis for a specified accuracy on a column of given length, a modified equation for the height equivalent

to the theoretical plate must be resorted to. It can be shown that

$$\frac{H}{L} = A' + B't + C'/t \quad , \tag{60}$$

where H is the height equivalent to the theoretical plate, t the duration of analysis, $A' = A/L$, $B' = B/L^2\Gamma_0$, $C' = C/\Gamma_0$, L is the column length, Γ_0 the overall Henry's constant for the most strongly sorbed component (the ratio of the amount of substance analysed in 1 ml of column volume to its concentration in the gas phase), and A, B, and C are constants of van Deemter's equation[20]. Hence, taking into account Eqn. (2), we have the expression

$$K^2 = \frac{0{,}045\,K_s^2}{A' + B't + C'/t} \quad . \tag{61}$$

Thus the choice of the phase is determined by the specified value of K, the selectivity, and the values of the terms A', B', and C', which depend on the efficiency, column length, and the sorption capacity. Fig. 8 shows different versions of K^2–t plots for two phases under comparison. It is evident that, depending on the specified degree of separation, either one or other phase may be preferable for a more rapid analysis. The time required to separate a two-component mixture for $K = 1$, can be calculated from the relation

$$\frac{t}{K_2} = 22{,}2\,\frac{\Gamma_0 H}{K_s^2 \bar{\alpha}} \quad , \tag{62}$$

where $\bar{\alpha}$ is the average linear flow rate of the carrier gas.

In the analysis of mixtures containing three and more components in the absolute majority of cases the separation factors for neighbouring peaks have different values. Thus, when $K = 1$ is selected for the pair least readily separated, there are "superfluous" sections of the zero line between other pairs corresponding to the excess time expended. The time from the instant of the introduction of the sample to the beginning of the elution of the first peak should be included in this also. If, other conditions being equal, the sorption capacity of the stationary phase is altered in such a way that all the components are separated with equal values of K, the duration of analysis becomes significantly smaller. In other words, on going from a two-component to a multicomponent mixture, the problem of selecting the optimum separation conditions becomes significantly more complex, because a new variable appears, which can be roughly represented by the change of the sorption capacity as a function of the sequential number of the peak on the chromatogram.

The problem of a quantitative estimate of the uniformity of separation was first examined by Peterson and Lundberg[101].

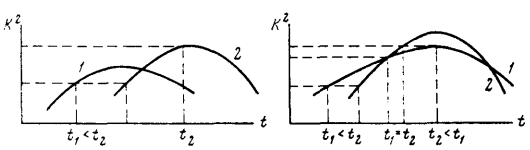


Fig. 8. Various versions on the graphical relation between the degree of separation K and the duration of analysis on a column of specified length with sorbents 1 and 2.

Criteria of the uniformity of separation and the "rapidity" of separation have also been recommended[5,102], whereby it is possible to take into account not only the characteristics determining the separation of two-component mixtures (selectivity, efficiency, sorption capacity) but also those which were previously estimated only qualitatively (uniformity of peak distribution in the chromatogram, desirability of using multistage systems, etc.).

The reduced criterion of uniformity $\bar{\Delta}$ is

$$\bar{\Delta} = \frac{n_k \tau K}{t} \quad , \tag{63}$$

where n_k is the number of peaks, τ the width of the least diffuse peak (in units of time) measured at the height corresponding to the required degree of separation (for example, when almost complete separation is necessary, this is the base of the peak), and K the degree of separation of the pair least readily separated.

The coefficient defining the rate of separation (the "rapid action" coefficient) can be formulated thus:

$$\lambda = \frac{n_k K^2}{t} = \frac{\bar{\Delta} K}{\tau} \quad . \tag{64}$$

The separation of a mixture of C_7–C_{10} straight-chain saturated hydrocarbons on columns containing phases of different polarity [squalane and di(β-cyanoethyl) sulphide] may be examined as an example of the use of λ for the selection of the stationary phase[67]. The corresponding chromatograms and plots of lg V^{rel} against n_C are shown in Fig. 9. The chromatograms were obtained under identical working conditions and for the same efficiency. Evidently best separation on columns of given length is attained with the nonpolar sorbent for which $b = 0.40$ and $k_s = 0.86$ (for the polar sorbent $b = 0.34$ and $k_s = 0.75$). However, if the duration of analysis is the decisive parameter, it is necessary to compare the coefficient defining the rate of separation. Then it was found that the separation of the mixture with the specified degree of separation can be carried out

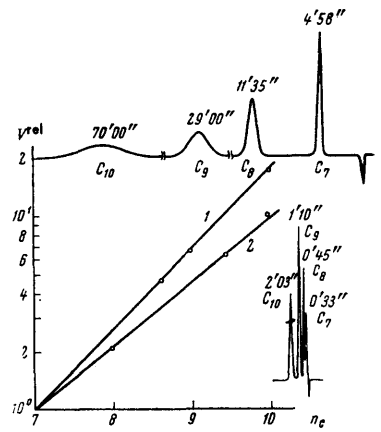


Fig. 9. Variation of the relative retention volumes of straight-chain saturated hydrocarbons with the number of carbon atoms in the molecule; stationary phases:
1) squalane; 2) di(β-cyanoethyl) sulphide; chromatograms obtained on a column 1.2 m long at 60°C and a carrier gas flow rate of 60 ml min^{-1}.

approximately 27 times faster on a column with the non-polar phase, since the "rapid action" coefficient λ is in this case 27 times larger.

If it is necessary to select a phase ensuring the most rapid analysis with a specified accuracy on a column of given length, then the choice depends on the corresponding value of K. If the value of K achieved on the polar phase for the least readily separated pair (heptane–octane) corresponds to the specified value, the polar phase is to be preferred; otherwise the non-polar phase must be chosen.

An estimate of the conditions of chromatographic analysis and, in particular, the suitability of a particular stationary phase for the solution of a concrete problem can be achieved using certain elements of information theory [103]. Thus a method has been proposed [105] on the basis of the concept of useful information [104], whereby it is possible to compare different versions of the analytical procedure. The information defect is the difference between the indeterminacy N_x obtained in the analysis and the entropy S, where

$$N_x = -\sum_{i=1}^{n_k-1} \frac{\psi_i}{\sum_{i=1}^{n_k-1}\psi_i} \mathrm{ld}\,\frac{\psi_{ie}}{\Sigma\psi_{i_e}}$$

and

$$S = \Sigma \frac{\psi_i}{\Sigma\psi_i} \mathrm{ld}\frac{\psi_i}{\Sigma\psi_i} \quad , \qquad (65)$$

ψ_i is the degree of separation of the ith pair of peaks required for the attainment of the specified accuracy, ψ_{ie} the experimental value of ψ, ld denotes a double logarithm, and n_k is the number of peaks. A decrease of the information defect is evidence that the conditions of analysis have become more satisfactory. Instead of ψ one can use other separation factors and also differences between the retention indices of neighbouring components.

6. BINARY SORBENTS

For an optimum separation of complex mixtures, sorbents with a rigorously defined selectivity are required. The problems in the selection of such sorbents can be successfully solved by using binary sorbents of controllable composition. Thus, in the separation of gaseous saturated and unsaturated hydrocarbons a column with a silver nitrate solution is used, but saturated hydrocarbons are eluted as a single peak. On the other hand, a column with the non-polar liquid paraffin does not always lead to a satisfactory separation of ethane from ethylene and of propane from propene, particularly when the detector exhibits significant inertia and the number of theoretical plates in the column is low¶. To achieve a clear separation of all the peaks it is desirable to connect the two columns in series [35].

Columns containing two (or several) individual sorbents can be prepared as follows: (a) sections with individual sorbents are joined in series (compound column); (b) individual stationary liquids are deposited on a solid carrier, the sorbents are mixed, and loaded into the column (column with a mixed sorbent); (c) a mixture of stationary liquids is deposited on a solid carrier (sorbent with a mixed phase).

The dependence of the elution characteristics of substances on columns with binary sorbents on the relative amounts of the individual stationary phases has been investigated by a number of workers [2,35,58,62,106–115]. In those cases where the pressure gradients are low the separation achieved on a compound column is almost identical with that on a column with a mixed sorbent. If the gradients are considerable, they influence the overall sorption characteristics. Thus the effective retention volume [4] of a component on a compound column is

$$V_N = V_{N_1}\frac{j}{j_1}\,\frac{p_{01}}{p_0} + V_{N_2}\frac{j}{j_2} \quad , \qquad (66)$$

where V_{N_1} and V_{N_2} are the effective retention volumes of the component on sections with the first and second sorbent, j the column pressure gradient factor [116], j_1 and j_2 are the pressure gradient factors in the first and second section, p_0 the pressure at the outlet from the column, and p_{01} the pressure at the boundary between the sections. Analogous relations hold also for other retention characteristics [113]. As a result of the influence of pressure gradients, a very interesting effect, first noted by Zhukhovitskii et al., [114] occurs in experiments with compound columns. A change in the sequence of the sections can result in a change of the degree of separation of the components and even in the elution sequence. This effect has been used, in particular, in the development of a method for the determination of the allene and methylacetylene impurities in the propane–propene fraction [117]. Indeed Figs. 10*b* and 10*c* show that with one sequence of the sections the allene and methylacetylene peaks merge into one, which is necessary to obtain a signal to be fed into the control system of the purification process of the propane–propene fraction, while with the reverse sequence the peaks are separated, which is desirable in laboratory analysis.

Graphical relations are used in the selection of the optimum composition of the sorbents; in the general case it is desirable to use for compound columns relations of the type shown in Fig. 10*a*. Here the retention characteristics (reduced retention time, reduced, effective, or specific retention volume) are plotted against the ratio of the reduced lengths of the sections [122], the reduced length of a section being defined thus:

$$L_{\mathrm{red}\,i} = L_i\frac{p_{oi}}{j_i} \qquad (67)$$

where L_i is the length of the section, p_{oi} the pressure at the outlet from the section, and j_i the pressure gradient factor in the given section.

When the effect of the pressure gradient is neglected, the ratio of the true lengths of the sections can be plotted along the abscissa axis. Thus by plotting along the ordinate axis the ratio (t_R/t_0) of the retention time of the given component to that of a non-sorbed substance, Rohrschneider [58] determined the optimum ratio of the lengths of the sections with diethylcyanamide and di(β-cyanoethyl) ether for the analysis of a mixture of C_1–C_5 hydrocarbons.

The corrected peak width on a compound column (ω, ml) can be determined from the following formula:

$$\omega^2 = \omega_1^2\frac{p_{01}^2}{p_0^2}\frac{j^2}{j_1^2} + \omega_2^2\frac{j^2}{j_2^2} \qquad (68)$$

where ω_1 and ω_2 are the corrected peak widths in the first and second sections. Similarly it is possible to calculate

¶ When a high-efficiency column with a non-polar sorbent is used, completely satisfactory, albeit non-uniform, separation of C_1–C_3 hydrocarbons is achieved [102].

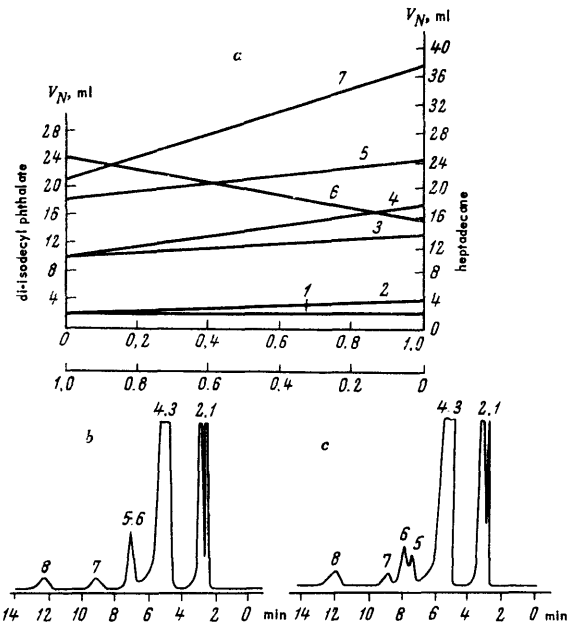


Fig. 10. *a*) Variation of the effective retention volume with the ratio of the effective lengths of sections with heptadecane and di-isodecyl phthalate; chromatograms of the propane–propene fraction on a compound column 7.1 m long;
b) order of sections: 2.4 m with heptadecane and 4.7 m with di-isodecyl phthalate;
c) reverse order; temperature 25°C: 1) ethylene; 2) ethane; 3) propene; 4) propane; 5) allene; 6) methylacetylene; 7) isobutane; 8) n-butane.

the number of theoretical plates, the selectivity coefficient, and the separation factor on compound columns [113]. Thus the degree of separation is defined by the equation:

$$F = \frac{\Delta V_R^2}{\omega_1^2 + \omega_2^2} = \frac{\left(\Delta V_{R_1}^0 \frac{p_{01} j}{p_{0} j_1} + \Delta V_{R_2}^0 \frac{j}{j_2}\right)^2}{\frac{\left(\Delta V_{R_1}^0 \frac{p_{01} j}{p_{0} j_1}\right)^2}{F_1} + \frac{\left(\Delta V_{R_2}^0 \frac{j}{j_2}\right)^2}{F_2}} , \quad (69)$$

where ΔV_R is the difference between the retention volumes of the components on the compound column, ω_1 and ω_2 are the peak widths, $\Delta V_{R_1}^0$ and $\Delta V_{R_2}^0$ are the differences between the corrected retention volumes in the first and second section, and F_1 and F_2 are the separation factors in these sections.

Calculations for columns with mixed sorbents are of course much simpler than for compound columns, because here the optimum ratio of the amounts of the individual sorbents is independent of the pressure gradient. Thus the specific retention volume on a column with a mixed sorbent is

$$V_g = \frac{g_1}{g} V_{g_1} + \frac{g_2}{g} V_{g_2} , \quad (70)$$

where V_{g_1} and V_{g_2} are specific retention volumes (ml g^{-1}) on columns with individual sorbents, $g = g_1 + g_2$, and g_1 and g_2 are the amounts (grammes) of the first and secondary stationary liquid.

The elution characteristics of columns with mixed phases are determined by logarithmic and not linear interpolation. Indeed the following equation follows from the equality of the free energies:

$$\lg V_g = \frac{g_1}{g} \lg V_{g_1} + \frac{g_2}{g} \lg V_{g_2} , \quad (71)$$

This relation is valid only when the excess entropy of the mixture of the two phases is zero [118]. Under the same condition the expression for the retention index is

$$I = I_1 \frac{g_1 b_1}{g_1 b_1 + g_2 b_2} + I_2 \frac{g_2 b_2}{g_1 b_1 + g_2 b_2} , \quad (72)$$

where b_1 and b_2 are the slopes of the plots of $\lg V^{rel}$ against n_C for the first and second phase and I_1 and I_2 are the retention indices on columns with the individual phases.

In conclusion of this section, the work of Porter et al., [119] in which the optimisation of the composition of the mixed phase is achieved with the aid of a computer, may be mentioned.

7. EFFECT OF TEMPERATURE ON THE SELECTIVITY OF THE PHASES; TEMPERATURE LIMITS OF THEIR APPLICATION

Since Henry's constants and also diffusion coefficients depend to a great extent on temperature, the latter is one of the principal factors which determine the duration of analysis, column selectivity, and the degree of spreading of chromatographic zones. Henry's constant (Γ) is known to be exponentially related to the reciprocal of the absolute temperature $1/T$ and therefore an increase of temperature greatly reduces the sorption capacity of the stationary phase.

Fig. 11 shows as an example a plot of the logarithm of the relative retention volume against the reciprocal of temperature† for certain saturated hydrocarbons and cycloalkanes on a column with 12 wt.% of tricresyl phosphate on Chromosorb [120]. Usually, when the temperature is increased, the straight lines corresponding to the individual components approach one another, which leads to a decrease of the selectivity coefficients. This is shown to a particularly high extent when polar forces operate.

However, certain anomalies are also encountered. Thus when a sorbent prepared by solidifying a polyester resin directly on the surface of a solid carrier is used, rapid analysis of a mixture of C_6–C_{10} hydrocarbons can be achieved at 25–30°C. [30] Under these conditions the sorbent exhibits moderate selectivity in the separation of saturated hydrocarbons and alkylbenzenes. When the temperature is raised, the selectivity increases significantly [121]. This is obviously because the sorbent exhibits both adsorption and absorption properties, the latter becoming enhanced at a higher temperature as a result of the decrease of viscosity.

Several papers [122–124] describe chromatographic separation on columns with phases having anisotropic properties and forming liquid crystals in certain temperature ranges. When the temperature is raised above a certain limit, the retention volume decreases sharply, because the phase passes into an isotropic state. The capacity of certain

† A relation of the type of the Antoine equation is more accurate in many cases: $\lg V^{rel} = A + B/(C + T)$, where A, B, and C are constants.

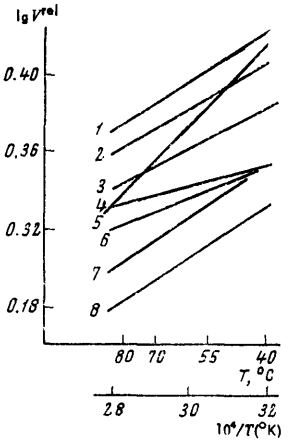


Fig. 11. Variation of the relative retention volume with the operating temperature of a column with tricresyl phosphate: 1) *trans*-1,2-dimethylcyclopentane; 2) *trans*-1,3-dimethylcyclopentane; 3) *cis*-1,3-dimethylcyclopentane; 4) cyclohexane; 5) heptane; 6) 1,1-dimethylcyclopentane; 7) 3-ethylpentane; 8) 2,2,4-trimethylpentane.

substances (in particular *pp*-azoxyphenetole) to form liquid crystals and exhibit selectivity at the same time have been used for the separation of the isomeric xylenes. It is also interesting to note that in many cases it is possible to alter the elution sequence of various substances by altering the temperature. Thus Fig. 11 shows that the position of the heptane peak alters relative to the peaks of the other substances as a function of the operating temperature.

If the values of Γ_S [see Eqn. (14)] for the components being separated are equal, the selectivity coefficient for the column is

$$K_c = \frac{2\varkappa_1\Gamma_S\left(e^{Q_2/RT} - e^{Q_1/RT}\right)}{2\varkappa + \varkappa_1\Gamma_S\left(e^{Q_2/RT} + e^{Q_1/RT}\right)} , \qquad (73)$$

where $\varkappa$ is the fraction of the column volume occupied by the gas phase, $\varkappa_1$ the fraction of the volume occupied by the stationary phase, Q_1 and Q_2 are the heats of solution, and R is the gas constant.

The following relation holds for diffusion in the liquid phase:

$$D_L = D_0 e^{-\beta Q/RT} , \qquad (74)$$

where D_0 is a constant and β the coefficient which can be assumed to be approximately 0.35. [125]

Analysis of theoretical and practical data shows that usually the degree of separation increases as the temperature is reduced, but this involves an increase in the duration of analysis. Evidently it is desirable to reduce simultaneously the operating temperature and the degree of impregnation [126,127], if the overall temperature dependence of the selectivity, sorption capacity, and efficiency indicates an increase of λ.

For a specified duration analysis, there exists an optimum temperature in each system corresponding to the maximum degree of separation. With decrease of the sorption capacity, the optimum temperature falls [82].

The range of operating column temperatures is known to be limited by the requirement that the stationary phase should be almost involatile. But it is recommended that the vapour pressure of the phase at the operating temperature should be not more than 0.5 mmHg (in certain cases a vapour pressure up to 10 mmHg is permitted). The ranges of the operating temperatures for columns with different phases have been tabulated [3,12], their limits being determined not only by the nature of the phase but also by the type of detector and other conditions [129-131]. Since the vapour pressure is related logarithmically to temperature, the "life time" of the column τ_k also decreases logarithmically with temperature. According to Kaiser [9], $\lg \tau_k = k/T$, where k is a constant.

The maximum operating temperature of sorbents with the stationary phases usually employed is such that losses during the first hour of the experiment do not exceed 1% of the total amount of the phase and in the "steady state" they do not exceed 0.1% (the larger losses during the first hour are due to the evolution of volatile impurities) [132]. Only in rare cases are more considerable losses permitted; for example, dimethylformamide, which exhibits high selectivity in the separation of saturated hydrocarbons and olefins, is highly volatile and even at 20°C the losses amount to about 3% per hour.

The method for the determination of the volatility of stationary phases is as follows [132]: 2.0 g of the stationary phase is mixed with 8.0 g of ignited refractory brick and placed in a weighed glass tube. The sorbent layer is compacted somewhat by tapping the tube, after which the tube is reweighed and closed on top by a layer of glass wool. It is then connected to a nitrogen supply and placed in a thermostat set at the required temperature. The flow rate of nitrogen is maintained at 15 ml min^{-1}. After an hour the tube is removed from the thermostat, the nitrogen supply is disconnected, and after being cooled in a desiccator the tube is weighed again. The losses during the first hour and the average losses in the course of the next three hours are recorded.

8. EFFECT OF THE STATIONARY PHASE ON THE SPREADING OF CHROMATOGRAPHIC ZONES

Since the peak width depends both on the sorption characteristic and on the diffusion coefficient in the liquid phase, it is evident that the nature of the stationary liquid phase and its operating conditions have a significant effect on the spreading of the chromatographic zones. Indeed the peak width of the elution curve is related to the width on the sorbent layer σ (cm) by the expression

$$\omega = \Gamma_0\sigma \simeq \Gamma_0\sqrt{LH} , \qquad (75)$$

where Γ_0 is the overall Henry's constant, H the height equivalent to the theoretical plate, and L the column length.

The effect of the stationary phase on the spreading of peaks within the limits of a homologous series has been examined by Turkel'taub [133], who established a linear relation between the logarithm of the peak width and the ratio of the boiling point of the substance to the column temperature. As a result of the proportionality between the peak width and the overall Henry's constant, a linear relation holds between the reduced peak width (the difference between the peak width of the component being analysed and the peak width of a non-sorbable substance) and the number

of carbon atoms in the molecule. This relation obtains also when the column efficiency changes significantly on going from one homologue to another.

If mass transfer by internal diffusion plays a decisive role in zone spreading, the degree of separation is $K' = (\frac{1}{2}\Delta V_R)/\omega_{0.5(1)}$, where ΔV_R is the difference between the retention volumes of adjacent homologues and $\omega_{0.5(1)}$ is the peak half-width of the first homologue, which is related as follows to the number of carbon atoms in the molecule:

$$\lg K' = a' + 0{,}5\, b \cdot n_c \quad . \qquad (76)$$

Here the constant b is the same as in Eqn. (33) and therefore the slope of the $\lg K'-n_C$ line is smaller by a factor of two than the slope of the $\lg V^{rel}-n_C$ line [5].

One of the requirements which must be met by the stationary liquid is that its viscosity should be low. This is quite reasonable when it is remembered that the viscosity is inversely proportional to the diffusion coefficient in the liquid phase. Thus Duffield and Rogers [134] showed that the efficiency of a column with Carbowax 400, whose viscosity is 102 cP (at 25°C), is significantly lower than that of a column with phenylacetonitrile, whose viscosity is 1.98 cP. Quantitative relations characterising the effect of viscosity on efficiency have been given in a number of papers [5,130,135].

If it is assumed that column efficiency is determined solely by internal-diffusion mass transfer, the ratio of the "rapid action" coefficients for two stationary liquids is

$$\frac{\lambda_2}{\lambda_1} = \left(\frac{K_{s2}}{K_{s1}}\right)^2 \left(\frac{\Gamma_{02}}{\Gamma_{01}}\right)^2 \frac{\Gamma_1}{\Gamma_2}\frac{\zeta_1}{\zeta_2}\left(\frac{M_2}{M_1}\right)^{0.5} \frac{\Gamma_{n.1\,(n)}}{\Gamma_{02\,(n)}} \quad , \qquad (77)$$

where the subscripts 1 and 2 refer to the stationary phases, K_s are the selectivity coefficients for the least readily separated pairs, the subscript n refers to the last component, ζ is the dynamic viscosity, and M the molecular weight of the phase. This relation makes it possible to estimate the gain as regards duration of analysis, associated with the selection of a phase having a low viscosity. Examples of the employment of such phases are the rapid analyses on columns with adiponitrile and straight-chain saturated hydrocarbons [5,102].

The data reviewed thus show that, by taking into account the physicochemical characteristics of stationary phases and various relations between them and the retention and spreading parameters, it is possible to solve successfully the problems involved in the selection of the optimum conditions for chromatographic separation.

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STUDY OF MOLECULAR MOTION IN SOLID POLYMERS BY THE INTERNAL FRICTION METHOD

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I. INTRODUCTION

Various properties of solid polymers depend decisively on the nature of the motion of the individual groups and segments of the molecular chains from which they are built up. Therefore it is both of practical and theoretical importance to know the type of molecular motion occurring in the given polymer and the dependence of the type of motion on the composition, structure, molecular weight, temperature, and other factors. One of the most useful physical methods for the investigation of the internal motion of polymeric chains is the internal friction method, the essential features of which are as follows.

When a body is deformed, internal forces (or stresses) arise, due to the change in the distribution of molecules or atoms in it. If the stresses and the relative deformations throughout the period of operation of external forces remain constant and fall to zero instantaneously when the operation of such forces ceases, then we are dealing with a perfectly elastic substance. The isothermal state of such a substance, if the latter is isotropic, is known to be described by the generalised Hooke's law[1]:

$$\sigma_{ik} = 2G\left(u_{ik} - \frac{1}{3}\delta_{ik}u_{ll}\right) + K \cdot u_{ll} \cdot \delta_{ik}\,, \qquad (1)$$

where $\dot{u}_{ik} = 0$ when the external forces are constant. Here σ_{ik} is the elastic stress tensor, u_{ik} the deformation tensor, and G and K are the moduli of shear and bulk elasticity respectively.

It is possible also to imagine another ideal case, where the relative deformations of the substance are not constant under the action of constant external forces, but increase continuously at a particular constant rate which is proportional to the stress. The behaviour of such an ideally viscous isotropic material is described[1] by the generalised Newton equation:

$$\sigma'_{ik} = 2\eta\left(\dot{u}_{ik} + \frac{1}{3}\delta_{ik}\dot{u}_{ll}\right) + \zeta\dot{u}_{ll} \cdot \delta_{ik}\,, \qquad (2)$$

where σ'_{ik} is the dissipative stress tensor, $\dot{u}_{ik}$ the derivative of the deformation tensor with respect to time, and η and ζ are the shear and bulk viscosities.

However, in no real substance with a definite structure can stresses exist indefinitely or decrease instantaneously, since during deformation the structure of the substance changes continuously (and in a complex manner) at a certain finite velocity, determined by the nature of the substance. Therefore the behaviour of a real material is in fact described by more complex relations than Eqns. (1) and (2).