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# Physicochemical application of capillary chromatography

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ABSTRACT. The application of capillary gas chromatography in the determination of the free energy, enthalpy, and entropy of sorption, the saturated vapour pressure and activity coefficients, the assessment of the lipophilicity of volatile compounds, and the study of the properties of polymers and liquid crystals is described. The use of reaction capillary chromatography in kinetic studies of conformational conversions, thermal degradation, and photochemical reactions is examined. Studies on the use of capillary columns for determination of the second virial coefficients and viscosity of gases and the diffusion coefficients in gases, liquids, supercritical fluids, and polymers are analysed.

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## I. Introduction

High-performance capillary chromatography is a powerful method for the analysis of multicomponent mixtures in chemistry, biology, and medicine and in the monitoring of environmental pollution. Furthermore, the practical value of this type of chromatography is not purely restricted to analytical problems, as it is also a convenient method for the determination of physicochemical parameters, for which packed columns are traditionally used.[1–4] However, with regard to their physicochemical applications, capillary columns have a whole series of advantgages over packed columns, and in recent years they have been increasingly used for the determination of the thermodynamic properties of sorption, the study of the transport properties of gases and liquids, research on polymers and liquid crystals, and also in chemical kinetics.

Open tubular or capillary columns (CCs) were first proposed by Golay.[5,6] They are relatively narrow and long, coiled cylindrical tubes in which the stationary phase is distributed over the inner surface of the walls. Golay pointed out that the main characteristic of CCs is not the small magnitude of their internal diameter (50–800 μm) but their hollowness, which provides them with high permeability.[7] Because of the low pneumatic resistance of capillary columns it is possible to increase their length to 100 m or more and thus increase their efficiency approximately by a factor of $10^2$ compared to packed columns. As a result, the accuracy in measuring retention parameters in capillary chromatography is 5–10 times greater than in chromatography with packed columns.[8] The high efficiency of CCs makes it possible to study several compounds in mixtures at the same time and to reduce the need for sample purity. When using capillary column for research, it is sufficient to have microgram quantities of the materials: micrograms of stationary phases and nano- or even pico-grams of volatile sorbates. Because of the lower sorptive capacity of CCs in comparison with packed columns and also their lower adsorption and catalytic activities, it is possible to study low-volatility, thermally labile, and chemically unstable compounds.[9–10] The extremly simple geometry of capillary columns and the possibility of preparing a readily controlled layer of the stationary phases make them ideal for measurement of diffusion coefficients in gases, liquids, and polymers. The aim of this review is to summarise the experience of using capillary columns in physicochemical studies.

## II. Determination of equilibrium sorption parameters and related values

Of fundamental importance in gas chromatography is the distribution coefficient of compounds in the system mobile phase–stationary phase, which may be calculated from the chromatographic retention and volumetric phase ratio. From the distribution coefficient and its dependence on temperature and pressure it is possible to determine thermodynamic parameters of sorption, such as the free energy, enthalpy and entropy of sorption, the activity coefficient of the sorbate at infinite dilution in the stationary phase, the saturated vapour pressure and volatility of the sorbate, and finally the mixed second virial coefficient of the sorbate–carrier gas intermolecular interaction.[3]

Sources of systematic errors not orginating from the equipment in the determination of these parameters can result from nonlinearity of the sorption isotherm, solubility of the carrier gas in the liquid phase, nonequilibrium solution of the compound and its adsorption at the phase boundaries of gas–liquid and liquid–phase wall of capillary column.

### 1. Determination of differential molar free energies of solution

Golovnya and Samusenko[11–13] studied the change in Gibbs potential when different classes of organic compounds were dissolved in poly(ethylene glycol) PEG 40M deposited on the walls of glass CCs that had been deactivated with KF and $Na_3PO_4$ salts. By calculating the differences in free energies of sorption of compounds with and without the functional groups $NO_2$, OH, $NH_2$, Br, SH and $CH_3$ it was possible to eliminate the undetermined factors related to

the phase ratio in the columns:

$$\delta(\Delta G)_{X,H} = \Delta G_{RX} - \Delta G_{RH} = -RT\ln\left(\frac{t_{RX}-t_M}{t_{RH}-t_M}\right) = -RT\ln(t'_{RX}/t'_{RH}), \quad (1)$$

where $t_{RX}$ and $t_{RH}$ are the retention times of compound RX with functional group X and its hydrocarbon analogue RH (n-octane or benzene), $t_M$ is the hold-up time, $t'_{RX}$ and $\tau'_{RH}$ are the adjusted retention times of compounds RX and RH. It was established that the presence of salts and their chemical nature affect the retention of compounds with functional groups that can undergo a specific intermolecular interaction. Unfortunately, it is not clear whether this interaction occurs with ions dissolved in PEG 40M or whether it takes place on the surface of the salt crystals by an adsorption mechanism. The same method was used on glass CCs with the stationary phases OV-101, OV-17, PEG 40M and added KF to determine the increments of methyl groups to the sorption potentials of methylbenzenes,[13,14] methylpyrazines,[15] methylpyridines, methylpiperidines, and branched secondary aliphatic amines.[14,16] From the relationships that were established, the authors developed schemes to predict the retention indices of methylpyrazines[15] and methylpyridines[17] for their identification on columns of varying polarity.

Grigor'eva et al.,[18,19] by using glass CCs with a thick layer of immobilised siloxane SE-54, studied the change in free energy of sorption of mono- and bi-functional carbonyl-containing compounds in relation to the number of their methylene units. An anomalously small retention of the primary homologues was detected for series of methyl and butyl n-alkyl ketones and fatty acid methyl esters. A similar pattern occurs for a series of dimethyl series of α,ω-dicarboxylic acids. The anomalies in the retention of the primary homologues in the above series were not observed when the more polar stationary phases OV-210, PEG 40M, SP-2300 and Silar 10 C were used.

## 2. Determination of the enthalpy and entropy of sorption

The heat of solution of a sorbate can be determined by studying its retention at different temperatures. On incorporating the Karger relationship:[20]

$$\Delta G = -RT\ln K = -RT\ln(k\beta), \quad (2)$$

the Gibbs–Helmholtz equation can be given in the form:

$$-R\left[\frac{\partial(\ln k\beta)}{\partial(1/T)}\right]_p = \Delta H, \quad (3)$$

where the heat of solution is determined as the gradient of the tangent to the curve of the logarithm of the capacity factor ($k$) against temperature on $-R\ln k$ and $1/T$ coordinates. It is worth noting that it is not necessary to know the distribution coefficient $K$ in order to determine $\Delta H$, since the phase ratio (β) is virtually independent of temperature.

A number of authors[21,22] determined the heat of solution of light aliphatic and alicyclic hydrocarbons ($C_5$–$C_8$) in squalane by using copper and steel capillary columns. When precise measurements of the absolute molar heats of solution were carried out,[22] the linear dependence of the enthalpy of solution on temperature and the nonideality of the gas phase were taken into account (see Section 3). By careful maintenance of a constant temperature (±0.01 °C) and pressure at the column inlet (±0.001 atm), the error in determination of $\Delta H$ was not more than 3%. Although the hydrocarbons studied are not very susceptible to adsorption, the latter may in principle affect the accuracy in determination of heats of solution since metal CCs have high adsorptive activity. Moreover, their extensive irregular surface[23] is difficult to cover completely with the stationary phase.

Mohnke and Heybey[24] determined the specific retention volumes of permanent gases and methane in glass CCS with zeolite 5A at different temperatures, and from them calculated the enthalpies of adsorption $\Delta H_{ads}$. In addition they determined the differences between the enthalpies and entropies of adsorption of methane and deuteromethane on a capillary columns with a layer of activated charcoal. Suslov et al.[25] determined the retention indices of hydroxy and amino derivatives of adamantane on glass capillary columns with OV-101 and XE-60 at different temperatures. By using the formulae proposed in two earlier studies,[26,27] Suslov et al.[25] calculated the free energies, enthalpies, and entropies of sorption of the adamantane derivatives from the derived values of the indices and experimental specific retention volumes of n-alkanes.

Berezkin and Korolev[9,10] estimated the error in the gas chromatographic determination of the heats of solution of compounds with varying polarity in thin layers of immobilised siloxane SE-30 resulting from their adsorption on the walls of quartz CCs. By using the "internal standard" method,[28] the authors[9,10] determined the true distribution constants for a number of compounds in the system gas–liquid phase at four temperatures, and from these values they calculated the true heats of solution of these compounds in SE-30. Furthermore, from the chromatographically determined distribution constants of the compounds in the system mobile phase–stationary phase they determined the apparent heats of solution of the same compounds while neglecting adsorption. Comparison of the true and apparent values showed that neglect of adsorption led to a 13–20% overestimation of the experimental heats of solution of polar compounds, while for n-tridecane this difference was 4%. This relatively large contribution of adsorption for polar compounds may be due partly to the low thickness of the phase layer (74 nm) and partly to the effect of the benzoyl peroxide used as an initiator for immobilisation of SE-30.[9,10] The use of this initiator is known to result in a considerable increase in adsorption activity of capillary columns with alkylpolysiloxanes.[29–30]

## 3. Effect of the nonideality of the gas phase on the equilibrium sorption parameters and a determination of the second virial coefficients of gases

As has already been mentioned, it is necessary to take into account the nonideality of carrier gases in precise physicochemical measurements. This manifests itself particularly clearly in high-performance capillary gas chromatography. Thus, replacement of the "completely ideal" carrier gas $H_2$ by $N_2$ produces such a marked change in selectivity for separation of the components of a sample of gasoline on a CC with a poly(dimethylsiloxane) phase that inversion of the peak yield occurs.[31]

At medium pressure and when the carrier gas does not dissolve in the stationary phase, the distribution coefficient depends on the mixed second virial coefficient of sorbate and carrier gas $B_{SG}$:[32,33]

$$\ln K = \ln K^0 + \frac{2B_{SG} - V_S^\infty}{RT} p_o J_3^4, \quad (4)$$

where $K^0$ is the distribution constant at zero pressure of carrier gas, $V_S^\infty$ is the molar volume of sorbate in the stationary phase, $J_3^4$ is the pressure drop factor $\{J_3^4 = {}^3/_4[(p_i/p_o)^4 - 1]/[(p_i/p_o)^3 - 1]\}$, and $p_i$ and $p_o$ are the pressures at the inlet and outlet of the column respectively. In order to calculate the mixed second virial coefficient of sorbate–carrier gas, the second virial coefficient of the carrier gas

must be known.[31] The second virial coefficients frequently serve as reference values in calculations and design in many fields of science and technology.

Huang et al.[34] put forward an original method for the experimental determination of second virial coefficients of gases ($B_{GG}$) using CCs without a stationary phase. The viscosity of gases and the coefficient ($\alpha$) of the linear dependence of viscosity on pressure are determined at the same time as $B_{GG}$ with this method. By integrating Poiseuille's equation, in which the pressure and viscosity are presented in the form of exponential series, and neglecting the terms with a higher order of insignificance, Huang et al.[34] derived equation (5), which relates $B_{GG}$, $\alpha$, and the viscosity of a gas at zero pressure ($\mu_0$) with the experimental parameters:

$$\frac{64p_o u_o}{p_i^2 - p_o^2} = \frac{d^2(1 + B_{GG}p_o/RT)}{L \quad \mu_0}[1 - (\alpha + B_{GG}/RT)p_o J_2^3], \qquad (5)$$

where $p_o$ and $u_o$ are the pressure and velocity of gas at the column outlet, $p_i$ is the pressure at the inlet, $L$ and $d$ are the length and internal diameter of the column, $J_2^3$ is the pressure drop factor $\{J_2^3 = {}^2/_3[(p_i/p_o)^3 - 1]/[(p_i/p_o)^2 - 1]\}$. The experimental equipment comprises a system of two identical capillary columns that are connected via a valve. The pressures at the inlet and outlet of the system $p_i$ and $p_o$ are kept at a constant level, and the gas velocity is controlled by the valve, with readings taken from manometers between the columns before and after the valve. The authors proposed a simple graphical method for determining $B_{GG}$, $\mu_0$, and $\alpha$ from the experimental values of the pressures and flow rate of gas. The calculated error in the determination of $B_{GG}$ and $\alpha$ for compounds with a boiling point close to room temperature is not more than 1%. By varying the composition of the gas mixture, it is readily possible with this system to determine the concentration dependence of $B_{GG}$, $\mu_0$, $\alpha$, from which the intermolecular interaction potential in the gas phase can be calculated.[34]

## 4. Determination of the saturated vapour pressure of compounds with low volatility

In contrast to other methods, the gas chromatographic method of determining saturated vapour pressure does not require the compound under study to be highly pure, but on the other hand it can be used to record simultaneously the vapour pressures of several components that are present in very small quantities in mixtures. Virtually all the studies on the gas chromatographic method for determining vapour pressure on capillary columns are devoted to highly toxic materials that contaminate the environment. The method is based on the assumption that the adjusted retention time of sorbates ($t'_R = t_R - t_M$) is inversely proportional to their saturated vapour pressure. This assumption is only strictly valid for ideal solutions in which the environment of a molecule is similar to the condensed state of pure sorbate. Thus, this approximation is closer the greater the similarity between the molecules of volatile substances and the stationary phase.

It follows from the Clausius–Clapeyron equation for the vapour of substances that

$$d(\ln p_i^0) = (\frac{\Delta H_i}{\Delta H_{st}})\, d(\ln p_{st}^0), \qquad (6)$$

where $p_i^0$ and $p_{st}^0$ are the saturated vapour pressures of the substance under study and a standard, $\Delta H_i$ and $\Delta H_{st}$ are their heats of evaporation. In the approximation used, the relative retention of a pair of sorbates is inversely proportional to their relative volatility:

$$k_i/k_{st} = p_{st}^0 / p_i^0, \qquad (7)$$

and

$$\ln p_i^0 = \ln p_{st}^0 - \ln(k_i/k_{st}). \qquad (8)$$

Incorporating Eqn. (6), we can write

$$\ln(k_i/k_{st}) = (1 - \Delta H_i/\Delta H_{st})\ln p_{st}^0 - C, \qquad (9)$$

where $C$ is a constant.

A compound which is chemically similar to the substance being studied and having a known heat of evaporation, boiling point, or saturated vapour pressure is used as the standard.[35] It is assumed in this case that $(\Delta H_i/\Delta H_{st})$ is independent of temperature over a wide range. The values of the constants $(\Delta H_i/\Delta H_{st})$ and $C$ are determined graphically, by plotting the dependence of $\ln(k_i/k_{st})$ on $\ln p_{st}^0$ at different temperature. The required vapour pressure is calculated from the equation

$$p_i^0 = p_{st}^{0(\Delta H_i/\Delta H_{st})} \exp C, \qquad (10)$$

which follows from Eqns. (8) and (9).

The saturated vapour pressures of polychlorinated biphenyls were determined in a similar manner using a short glass CC (1 m × 0.25 mm) with an Apolane-87 phase.[36] Isobutyl 2,4,5-trichlorophenoxyacetate was used as the standard. The values of $p_i^0$ extrapolated to 25 °C were $2 \times 10^{-4} - 4.5 \times 10^{-6}$ mmHg. The error in determining $p_i^0$ was not more than 30%. However, at 25 °C the sorbates are solids, and therefore the derived vapour pressures will probably be somewhat overestimated, since all the calculations related to a gas-liquid equilibrium at the temperature of chromatographic separation (60–130 °C). The author's argument about the need to use the most nonpolar stationary phase is also questionable, since the sorbates are compounds with medium polarity. Subsequently, in order to determine the vapour pressure of organochlorine and polyaromatic compounds, Bidleman[37] used a quartz CC (1 m × 0.22 mm) with immobilised poly(dimethylsiloxane) BP-1 in addition to a column with an Apolane-87 phase. He used n-alkanes ($C_{18}$ and $C_{20}$) and dibutyl phthalate as standards. However, the use of dibutyl phthalate gave values of the vapour pressure of nonpolar sorbates that were too low, so it was recommended to use $C_{14}-C_{16}$ n-alkanes when $p_i^0 = 10^{-1}-10^{-2}$ mmHg and $C_{22}-C_{24}$ n-alkanes when $p_i^0 < 10^{-6}$ mmHg as standards.

In order to assess the accuracy of the gas chromatographic determination of $p_i^0$, the data obtained were correlated with known values of the saturated vapour pressure. Although the temperature of separation of the components on capillary columns is considerably lower than their boiling points, it may be assumed that the experimental values of vapour pressure ($p_{GC}$) do in fact correspond to the vapour pressures above supercooled liquids ($p_l$). The equilibrium vapour pressure above a solid ($p_{sol}$) at 25 °C may be calculated from the entropy of fusion $\Delta S_f$ and melting point $T_m$ of the compound respectively:[38]

$$\ln(p_l/p_s) = \frac{\Delta S_f(T_m - 298)}{298R}. \qquad (11)$$

Since the values of the entropy of sorption of a large number of compounds average out to 56.5 kJ mol$^{-1}$ deg$^{-1}$, in the calculations frequent use is made of the empirical equation of MacKay:[39]

$$\ln(p_l/p_s) = 6.8(T_m - 298)/298.$$

Bideleman[37] found that the experimental vapour pressure values ($p_{GC}$) correlate well, but in the majority of cases they do not match the saturated vapour pressure values ($p_l$) determined by other methods. The correlation coefficients of the linear relationship

$$\log p_{GC} = m \log p_l + b \quad (12)$$

for columns with Apolane-87 and BP-1 were 0.97–0.98, with the smallest deviation of $p_{GC}$ occurring for the column with Apolane-87.[37] However, the column with BP-1 proved more convenient for a determination of the vapour pressure of chlorinated derivatives of phenol and hydroquinone.[40] The relationship between $p_{GC}$ and $p_l$ which was derived for chlorophenol was used in a chromatographic determination of the saturated vapour pressure of chloroguaiacols, chloroveratroles, and 4-nonylphenol.[40]

Kim et al.[41] studied the effect of different experimental factors on the accuracy of the gas chromatographic determination of the saturated vapour pressures of 20 organophosphorus pesticides with different structures. Parathion, methylparathion, diazinone, and dibutyl phthalate were used as standards. The length of the capillary columns (from 1 to 27 m) and the nature of the nonpolar stationary phases (SE-30, SE-54, RSL-100) did not have much effect on the magnitudes of the experimentally determined vapour pressures. To achieve a relative standard deviation of less than 10% it was necessary to determine the retention coefficients at five or more temperatures at 5 °C intervals or at three temperatures at 15 °C intervals. Comparison of the vapour pressures derived by the gas chromatographic method with the vapour pressures determined by the gas saturation method showed that the greatest accuracy in the gas chromatographic determination of vapour pressure is achieved when a standard that is closest in nature to the components under study is used. The lowest accuracy was recorded in the determination of saturated vapour pressures of polar compounds and components that were solids at room temperature.[41]

By using a 75 centimetre-long CC with grafted poly[dimethyl-(5%)-diphenylsiloxane] DB-5 (0.25 μm), Eitzer and Hites[42] determined the saturated vapour pressures of a number of polychlorinated dibenzo-*p*-dioxins and dibenzofurans. *p,p'*-DDT, which is eluted in a similar manner to the components being studied, was chosen as the standard. The vapour pressure of DDT was repeatedly determined by independent methods. Like the components under study, DDT is detected using a high-sensitivity electron capture detector, which makes it possible to decrease the quantity of sample to a minimum and hence exclude the possibility of overloading short CCs.[38] The authors[42] established a good correlation between the derived vapour pressure values and the retention indices of the respective dioxins and dibenzofurans determined on a CC of the same type (DB-5).[43,44] From the correlative equation obtained it is possible to predict the saturated vapour pressures of many compounds of these classes from their gas chromatographic retention indices. A comparison of the vapour pressure values determined on a column with DB-5 with the values determined by other methods showed that the gas chromatographic method gives underestimated pressure values for dibenzo-*p*-dioxins and dibenzofurans with a low chlorine content and values that a overestimated for their highly chlorinated analogues.[42]

Hinckley et al.[38] also determined the saturated vapour pressure of a number of organochlorine and organophophorus compounds and phthalate esters, using *p,p'*-DDT as a standard. The vapour pressures were $10^{-2}$–$10^{-4}$ Pa (25 °C). The authors concluded[38] that the main reasons for the lack of agreement between the vapour pressure values determined by chromatography and by other methods lie in the experimental errors in the determination and also in differences between the activity coefficients and of the compounds being studied in the stationary phase. In general, ideality of the solutions in the stationary phase is not essential for the gas chromatographic method. It is only necessary that the degree of nonideality for the compound being studied and the standard is the same. Thus, equations (7)–(9) for nonideal solutions must contain the additional terms $\gamma_{st}/\gamma_i$ and $\ln(\gamma_{st}/\gamma_i)$ respectively, and the accuracy of this method depends on the similarity between the activity coefficients of the compound under study and the standard in the stationary phase. The authors concluded that the gas chromatographic method is of limited suitability for determining the saturated vapour pressure of polar compounds because of the difficulty in selecting a suitable polar standard due to the marked differences between the activity coefficients of polar compounds.[38]

## 5. Determination of activity coefficients

Lunskii and Paizanskaya[45] recently put forward a method for the determination of activity coefficients at infinite dilution from the retention indices and saturated vapour pressures of sorbates. The retention indices of hydrocarbons from the gasoline fractions of unfractionated condensates were determined on glass CCs with squalane and dinonyl phthalate. For compounds having similar activity coefficients, the dependence of the retention indices on the logarithm of the partial saturated vapour pressures comprises a series of parallel lines with the same slope, governed by the relative retention of the n-alkanes used to determine the retention indices. Points that correspond to compounds with a similar molecular structure lie on each straight line of this series. The activity coefficients are determined from the values of the intercepts on the y-axis. It is also necessary to know the saturated vapour pressure of the n-alkanes used and their activity coefficients in the stationary phases for the calculation. It was established from the data obtained that isoalkane and naphthenic hydrocarbons form athermal solutions in squalane while in dinonyl phthalate their activity coefficients decrease with increase in temperature. For aromatic hydrocarbons the reverse effect occurs when the phases are changed. Solutions of all these hydrocarbons in squalane exhibit negative deviations from Raoult's law, while in dinonyl phthalate both negative and positive deviations occur.[45]

## 6. Determination of the lipophilicity of volatile compounds

Lipophilicity is an important property of biologically active compounds, and it is frequently determined as the logarithm of the distribution constant ($\lg K$) of these compounds in the system octane–water. The direct determination of distribution coefficients of a very large number of chemical compounds investigated at regular intervals for biological activity is difficlt using a static method or reverse-phase liquid chromatography.

In order to make use of the extensive quantity of gas chromatographic data, Kuchar et al.[46,47] developed a method for the indirect determination of lipophilicity of homologous series of structurally similar compounds from their retention indices on nonpolar and polar capillary columns. The distribution constant in the system octanol–water can be represented as the product of the distribution constants in the systems octanol–gas and gas–water: $K_{o/w} = K_{g/w}K_{o/g}$. Unfortunately, gas chromatographic determination of distribution constants in these sytems is impossible because of the high volatility of water and octanol, so normal stationary phases (SFs) are used instead,

assuming a similarity between water and a polar SF (PSF) and between octanol and a nonpolar SF (NSF):

$$K_{o/w} \cong K_{g/PSF} K_{NSF/g},$$

$$\log K_{o/w} \cong \log(K_{NSF}/K_{PSF}) + A,$$

or

$$\log K_{o/w} = \log(V'_{R,NSF}/V'_{R,PSF}) + B,$$

where $A$ and $B$ are constants.

By further assuming a linear relationship between the adjusted retention volumes ($V'_R$) of the compounds and their retention indices ($I = \alpha \log V'_R + \beta$), it was possible to derive the relationship

$$\log K_{o/w} = CI_{NSF} - DI_{PSF} + E, \quad (13)$$

where $C$, $D$, and $E$ are constants. By using, on the one hand, a database of Kováts indices determined on quartz CCs with SE-30 phases [poly(dimethylsiloxane)] and OV-351 (a copolymer of poly(ethylene glycol) and nitroterephthalic acid) phases[48–50] and, on the other hand, the values of lipophilicity calculated by additive methods, the authors determined the coefficients in Eqn. (13) for a large number of homolytic series of aliphatic, olefinic and aromatic esters and their chloro and nitro derivatives.[46,47] It transpired that for groups of homolytic series of structurally similar compounds the coefficients in Eqn. (13) were similar, and their lipophilicity could be calculated approximately from the common correlative equations. The high statistical significance of these equations ($r$ = 0.921 to 0.999) is an indication of the suitability of the chosen column system for an indirect determination of lipophilicity. At the same time, the similarity between the systems SE-30–OV-351 and octanol–water is very arbitrary, and the retention volume is in fact related nonlinearity to the Kováts indices, especially for the primary members of the homolytic series.[51] Moreover, it was established that the Kováts indices on polar stationary phases cannot serve as parameters for the relative solubility of compounds since the n-alkanes used to determine them are retained to a significant extent through adsorption on the surface of the polar phase.[52–54] All these factors limit the applicability of this method to an approximate determination of lipophilicity.

The most accurate method of assessing the lipophilicity is a direct determination of the distribution constant in a static experiment. In order to determine the distribution coefficients of highly lipophilic compounds, Haky et al.[55] analysed the composition of the equilibrium water and octanol phases on a quartz CC with immobilised poly[phenyl-(5%)-methylsiloxane] DB-5. The internal standards used were anthracene and fluorene, which have well-established distribution coefficients. The recorded values of lipophilicity matched the literature data within the limits of experimental reproducibility (±0.2 units of $\log K_{o/w}$). Thus, by combining the distribution method with a quantitative analysis of the phases on a high-performance capillary column, it was possible to determine with reproducibility and accuracy the lipophilicity of compounds up to values of $\log K_{o/w}$ = 5.7.[55]

## 7. Study of the properties of polymers

The solubility of compounds in industrial polymers is of interest in terms of its technological, hygiene and sanitation, and toxicological aspects. Capillary columns have been used to study the solubility of organic copounds in polyisobutylene, poly(vinyl acetate), poly(dimethylsiloxane),[56,57] polystyrene,[58] and poly-ethylene.[59] It was established in three studies[56,57,59] that the specific retention volumes of organic compounds in high-molecular-weight polymers deposited in capillary columns is higher than in packed columns. The specific retention volumes of 13 organic compounds, including THF, alkanes, alkenes, and arenes in a relatively thick layer (~1.4 μm) of low-density polyethylene (LDPE), dynamically deposited on a CC made of stainless steel, were measured over a wide temperature range (50–175 °C).[59] Because of the significantly nonequilibrium nature of the sorption, the retention volumes were extrapolated to zero flow of carrier gas. From the experimental finding and a considerable quantity of literature data, it was possible to derive correlative equations that related the specific retention volumes on HDPE ($V_g$) at different temperature with the critical parameters of the sorbates:

$$\ln(V_g p_c/100) = a + b(T_c/T)^2, \quad (14)$$

where $p_c$, and $T_c$ are the critical pressure and temperature of the sorbates; $a$ and $b$ are constants. The correlation coefficients for equations of the type (14) are 0.991 and 0.987 for molten and rubbery LDPE. By using these equations, it is possible at given temperatures to determine the solublity of any nonpolar or medium-polar compounds in polyethylene when their critical pressure and temperature are known.

According to the results of Pawlisch et al.[58] the graphs of the dependence of exit time of the chromatographic peak maximum on the velocity of the carrier gas frequently have considerable curvature, and extrapolation to zero flow can lead to errors in the determination of true retention volumes. The same authors determined the retention volumes of benzene, toluene, and ethylbenzene on a glass CC with thick layers (7–12 μm) of polystyrene from the magnitudes of the primary peak features by means of numerical treatment of the computer signal. Subsequently the activity coefficients at infinite dilution and the Flory–Huggins interaction parameters $\chi_{1,2}$ for these compounds were calculated from the specific retention volumes.

Barrales-Rienda et al.[60] recently determined the specific retention volumes of $C_9$–$C_{13}$ n-alkanes and $C_6$–$C_{10}$ aliphatic alcohols in poly[*N*-(n-octadecyl)maleimide] at different temperature. The polymer was deposited on a steel CC (resulting thickness of layer 1.67 μm) using a static method. From the data obtained the authors calculated the actvity coefficients at infinite dilution, the Flory–Huggins parameters $\chi_{1,2}$, and the solubility parameters $\delta_1$ and $\delta_2$. Furthermore, the temperature dependences of the activity coefficients and specific retention volumes were used to determine the partial molar heats of mixing and solution, the sum of which corresponded to the heats of evaporation of the pure sorbates, as calculated from the Clausius–Clapeyron equation. In a similar manner Roth et al.,[61] using glass CCs, determined the excess molar enthalpies of solution of $C_8$–$C_{12}$ n-alkanes in polysiloxanes. It was found that the values of the excess enthalpies of solution in poly(dimethylsiloxane) SE-30 were positive, while in poly[methyl-n-alkyl($C_8$–$C_{18}$)siloxanes] they were negative, which was an indication of the stronger intermolecular interaction between n-alkanes and polysiloxanes having long aliphatic side chains.

## 8. Study of the properties of liquid crystals

Liquid-crystalline compounds are used in gas chromatography as stationary phases that have unique selectivity towards stereoisomers. In a sense liquid-crystalline phases combine the high capacity of stationary phases with the structural selectivity of adsorbents.

Kirst et al.[62] studied the temperature dependences of the structural selectivity, capacity, and efficiency of copper CCs (40 m × 0.35 mm) with *p,p'*-methoxyethoxyazoxybenzene (MEAB), *p,p'*-azoxyphenetole (AOP), and their eutectic mixture. The

temperatures of maximum structural selectivity, determined from the ratio of the adjusted retention times of *p*- and *m*-xylenes, do not coincide with the temperatures of maximum capacity. The efficiency of the columns increases with temperature. MEAB displays the most favourable combination of these parameters on which the separation of *p*- and *m*-xylenes is dependent. The structural selectivity of the liquid-crystlline phases in capillary columns, as in packed columns, decreases with the thickness of their layers.[62]

Andronikashvili et al.[63] studied the possibility of measuring the temperatures of phase transitions of liquid crystals in steel and copper CCs (50 m × 0.25 mm). The above-mentioned MEAB and *p*-ethoxybenzylidenetoluidine (EBT) were used as the liquid-crystalline phases, It was established that the solidification temperatures of the nematic mesophases are virtually independent of the quantity of phases in the columns and the wall material. The mesomorphic–isotropic transition temperature ($T_{M\text{-}I}$) of MEAB varies by 15 °C with a change in quantity of this phase. The wall material of the columns affects the values of $T_{M\text{-}I}$ of the phases studied in different ways. Thus, on changing from steel columns to copper columns the mesomorphic–isotropic transition temperature for MEAB decreases by 8 °C while for EBT it increases by 27 °C.

The same authors determined the contribution of adsorption to the retention of organic compounds on a liquid-crystalline phase. The "internal standard" method, which assumed in particular that the surface of the walls was completely covered by the liquid-crystalline phase and that the gas–SF boundary remained unchanged on varying the proportion of the latter, was used.[28] Benzene was used as a nonadsorbing standard. It was found that the adsorption of toluene, ethylbenzene, *m*-, *p*-, and *o*-xylenes amounts to 3% of their retention values on MEAB at 95 °C. The contribution of the adsorption of n-alkanes ($C_6-C_8$) is an order of magnitude less.[63]

*N,N'* Bis(*p*-butoxybenzylidene)-α,α'-bis(*p*-toluidine) (BBBT) was treated as the stationary phase for the separation of isomeric tricyclic and tetracyclic polyaromatic hydrocarbons on stainless steel CCs.[64] The temperature dependence of the capacity of the column in the nematic mesophase region of BBBT was studied.

Russo et al.[65] recently investigated glas CCs with liquid-crystalline phases on layers of graphitised carbon and kaolin deposited on the internal walls. The phases used were *p,p'*-azoxydiphenetole (ADP) and the above-mentioned BBBT. A study was made of the stereoselectivity and efficiency of the columns in relation to the nature of the support, quantity of the phases, and temperature. It was found that on lowering the temperature, with BBBT changing from a nematic state to a smectic state, the coefficient of selectivity for separation of phenanthrene and anthracene decreased slightly, but because of the accompanying increase in viscosity of BBBT the efficiency of the columns decreased sharply. The use of kaolin has a marked stabilising effect on the efficiency of columns with BBBT and reduces the lower temperature limit by 40 °C for using columns with ADP. Thus, the use of adsorbents as supports is promising in terms of increasing the range of working temperatures and increasing the service life of capillary columns with liquid-crystalline stationary phases.

## III. Application of capillary gas chromatography in chemical kinetics

### 1. Reaction capillary chromatography

Reaction gas chromatography has found extensive application in chemical kinetics.[1–4] Chemical reaction in the columns takes place in parallel with chromatographic separation of its products, which assists their detection and identification using sensitive and selective detectors.[66] Capillary columns are closer to the ideal model of a chromatographic reactor than packed columns, and they can be used to separate the chromatographic zones of the reaction products and the initial reactants more completely, thus assisting a study of the section of the chromatogram lying between them which characterises the reaction occurring in the column.[67]

Möller et al.[68] examined the possibility of using reaction capillary gas chromatography for a determination of thermodynamic and kinetic reaction parameters. The decomposition of dicyclopentadiene in a 60 metre-long copper CC with a Flugizon phase was studied at 189–207 °C.[69] The extent of reaction was assessed from the decrease in area of the peak due to dicyclopentadiene eluted from the column:

$$m_0/m = \exp(k_{exp} t'_R), \quad (15)$$

where $m_0$ and $m$ are the quantities of dicyclopentadiene before entry and after exit from the column, $k_{exp}$ is the experimental rate constant of reaction, $t'_R$ is the adjusted retention time of dicyclopentadiene. Unfortunately, decomposition occurs simultaneously in both the stationary liquid phase and the carrier gas, which complicates a determination of the rate constants in each of these phases. The value of $k_{exp}$ that is determined experimentally comprises a total rate constant in each of the phases:

$$k_{exp} = k_{SF} + (t_{CG}/t_{SF})k_{CG}, \quad (16)$$

where $k_{CG}$ and $k_{SF}$ are the rate constants of reaction in the carrier gas and stationary phase, $t_{CG}$ and $t_{SF}$ are the residence times of the reactant in the carrier gas and SF, which correspond to the hold-up time and adjusted retention time $t_M$ and $t'_R$. In order to determine $k_{CG}$ and $k_{SF}$, it was necessary to vary the phase ratio in the column, which was achieved by blowing off Flugizon at a high temperaure. Flugizon is a mixture of alkylnaphthalenes, so that after blowing off it is most probable that not only the phase ratio changes but also the actual composition of the stationary phase is altered. The authors calculated the rate constants for decomposition of dicyclopentadiene in Flugizon ($k_{SF}$) at different temperatures, but to calculate the activation energy they used hypothetical rate consant values ($\bar{k}$), which were determined by assuming that the rate constants of reaction in the carrier gas and SF were equal:

$$m / m_0 = \exp(\bar{k} t_R), \quad (17)$$

where $t_R$ is the unadjusted retention time of dicyclopentadiene. The rate constants of reaction in the carrier gas and SF differ, and this approach results in errors. Furthermore, the kinetic data may be distorted because of the high catalytic activity of the copper surface of the capillary column.

### 2. Study of conformational conversions

Lai et al.[67] used quartz CCs (60 m × 0.2 mm and 25 m × 0.3 mm) with poly(dimethylsiloxanes) OV-1 and CP-Si15 to study the kinetics of conformational conversions in 9,10-bis(2,3-dimethylphenyl)phenanthrene. At 225 °C the *syn* and *anti* isomers of 9,10-bis(2,3-dimethylphenyl)phenanthrene are completely separated, while between them on the chromatogram there is a relatively long empty section of the zero line corresponding to the absence of conformational conversion between the isomers. On increasing the temperature the section between the peaks rises. The peak areas correspond to the number of molecules not participating in conformational conversions while the area of the elevated section between the peaks represents the number of molecules undergoing

conformational conversion in the column. With a decrease in velocity of the carrier gas the residence time of a sample in the hot column increases, and the number of molecules participating in conformational conversions increases. The rate constants for the forward and reverse *syn* → *anti* conversion were calculated from the decrease in peak area of the respective conformer with an increase in its residence time in the column. The values of the rate constants determined at different temperatures were used to calculate the activation energies of the forward and reverse conversions, which were 145 and 115 kJ $mol^{-1}$ respectively. Since, in the opinion of Lai et al.,[67] the conformational conversions probably occur only in the stationary phases, it would be more appropriate to use in the calculations the adjusted retention times, corresponding to the residence of the conformers in the SF (the reaction zone), rather than the total residence time of the isomers in the columns.

The same authors recently studied the kinetics of isomerisation of acetal, butanal, and isobutanal oximes, as well as sterically hindered methylphenylanthracenes and phenanthrenes on CCs with a dimethylsiloxane phase and FFAP.[70] In order to simplify the calculations it was assumed that the rate constants of isomerisation in the carrier gas and SF were equal. The Arrhenius method was used to determine the activation energies, which constituted 100–140 kJ $mol^{-1}$ for the rotational isomerisation of methylphenylanthracenes and phenanthrenes and about 70 kJ $mol^{-1}$ for *syn* ⇄ *anti* conversions of oximes. Lai et al.[70] concluded that it is only possible to determine the conversion barrier in those cases where the initial concentration of a conformer in a binary mixture is not less than 5%.

### 3. Study of photochemical reactions

A glass capillary column is an ideal reactor for studying photochemical reactions on the surface and in thin layers. The absence of packing and the transparency of the walls permit the free access of radiation to photolabile compounds.[66] In CCs it is possible to deposit different nonvolatile supports and layers and readily batch small quantities of volatile compounds and thus study various photochemical reactions between them.

Laster et al.[66] tested the suitability of glass CCs (10 m × 0.3 to 0.5 mm) for a study of photochemical processes at the gas–solid support phase boundary in a gas adsorption form of chromatography. The photochemical demethylation of dimethylaniline adsorbed on the surface of alizarin was studied as a model. The latter was deposited on the "fluffy" internal surface of a capillary column obtained by etching the walls with 2-chloro-1,1,2-trifluoroethyl methyl ether.

Alizarin, like other anthraquinone derivatives, has strong electron-withdrawing properties in its excited triplet state. Samples of dimethylaniline vapour were introduced either in batches or continuously using a T-shaped diffusion saturator. On irradiation of the CC of the chromatograph in a thermostat with visible light from a halogen lamp, the peak due to dimethylaniline disappeared and in its place a peak due to the product of the photochemical reaction subsquently appeared, identified by chromatography–mass spectrometry as methylaniline. It was established that the frontal method with continuous introduction of sample vapour achieved a higher sensitivity and reproducibility than the development method with batched introduction of sample. In the frontal method a variant of vacancy chromatography occurs. After irradiation with light, two peaks appear at the outlet of the column—a negative vacancy peak due to decomposed dimethylaniline and a positive peak due to the reaction product. The logarithm of the dependence of the degree of reaction on the intensity and duration of column irradiation and the linear dependence on the concentration of the initial reactant indicated that the reaction was first-order with respect to dimethylaniline.[66]

## IV. Study of the transport properties of different media

In order to measure diffusion coefficients in gases, liquids, and supercritical fluids, capillary columns without stationary phases are used, while for measurement of diffusion coefficients in polymers the latter are deposited as a uniform layer on the inner walls of capillary columns. The advantages derived from the methods of measuring diffusion coefficients using chromatographic equipment are the simplicity of instrumentation, high output, relatively high accuracy, and the possibility of studying diffusivity under conditions of limiting dilution.

The theory of dispersion of the zones of a nonsorbing compound in hollow cylindrical tubes was developed by Taylor[71] and Aris.[72] The height equivalent to a theoretical plate (HETP), which represents the dispersion of a zone, is defined as the sum of two components, the first of which is due to longitudinal diffusion of a compound in the mobile phase (MP) while the second results from resistance to mass transfer due to the parabolic nature of the flow profile of the MP in a cylindrical tube:

$$H = \frac{2D_{m,o}}{u_o} + \frac{d^2 u_o}{96 D_{m,o}}, \qquad (18)$$

where $H$ is the height equivalent to a theoretical plate, $D_{m,o}$ is the diffusion coefficient in the MP at the column outlet, $u_o$ is the velocity of the MP at the outlet, $d$ is the internal diameter of the column. For a Gaussian elution curve the HETP is defined as

$$H = \frac{L}{N} = \frac{L}{5{,}45} \frac{(W_{0,5})^2}{t_R}, \qquad (19)$$

where $L$ is the length of the column, $N$ is the number of theoretical plates, $t_R$ and $W_{0.5}$ are the exit time of the peak maximum and its width at the half-height. Having determined the value of the HETP, $D_{m,o}$ is calculated from Eqn. (18):

$$D_{m,o} = \frac{u_o}{4}(H \pm \sqrt{H^2 - d^2/12}). \qquad (20)$$

The sign in front of the square root in Eqn. (20) is usually negative, except when a gas with low flow rates is used as the MP.

### 1. Determination of diffusion coefficients in gases

Tubes with a diameter of 4–5 mm are mainly used to determine diffusion coefficients in gases ($D_g$).[73–75] When working with capillary columns both a continuous elution method[76] and a stopped flow method[77] have been used.

At the optimum flow rate of gas ($u_{opt}$) the values of HETP are at a minimum, and the parameter $u_{opt}$ is simply related to the diffusion coefficient of the compound in the gas and the internal diameter of the column:

$$u_{opt} = (8\sqrt{3D_g}) / d. \qquad (21)$$

Using Eqn. (21), Knox and McLaren[78] determined $d_g$ for ethylene in nitrogen from the value of the optimum flow rate in a capillary tube made of nylon (16.64 × 0.88 mm). The continuous elution method

has high output but at the same time it is necessary to have a precise knowledge of the internal diameter of the column and to take into account extracolumn dispersion of the zone, which in the case of using CCs may be fairly considerable.[78,79] In a subsequent study[77] the same authors put forward an alternative chromatographic method for determining $D_g$ which avoids these difficulties. In this method, when the zone of diffusant approaches the centre of the column the flow of carrier gas is stopped and broadening of the zone occurs solely through longitudinal diffusion, which is proportional to the duration of flow stoppage ($\theta$) and the diffusion coefficient of the component in the gas:

$$\sigma_l^2 = 2D_g\theta, \tag{22}$$

where $\sigma_l^2$ is the variance of the zone in units of length. After an interval of time $\theta$ the flow of gas is restored. The variance of the zone in time units ($\sigma_t^2$) recorded by the detector at the column outlet is made up by the extracolumn variance ($\sigma_{ec}^2$), the variance of the zone in a column by movement of gas ($\sigma_c^2$), and the variance of the zone throughout the period of flow stoppage ($\sigma_\theta^2$):

$$\sigma_t^2 = \sigma_{ec}^2 + \sigma_c^2 + \sigma_\theta^2. \tag{23}$$

The variance of the peak is measured for different durations of flow stoppage ($\theta$ varies from 1 to 20 min). The $\sigma_{ec}^2$ and $\sigma_c^2$ variances do not depend on the value of $\theta$. Thus, a graph of the variance of the peak against the duration of flow stoppage is a straight line from whose slope the diffusion coefficient is determined ($\tan\alpha = 2D_g/u_O^2$). $D_g$ for ethylene in nitrogen was determined to an accuracy of 2% with this method using nylon tubes (8.34 m × 0.88 mm and 16.40 m × 0.88 mm).[77] A limitation of this method is the need for a small pressure drop in the tube. Thus, with a pressure difference of more than 20 mmHg the velocity of gas cannot be normalised up to the time of peak exit, which results in an overestimated value of the experimental diffusion coefficient.[77]

With a low velocity of carrier gas in a tube of small diameter the contribution of longitudinal diffusion to dispersion is much larger than that of resistance to mass transfer in the gas, and the second term in Eqn. (18) can be neglected:

$$H = 2D_{g,o}/u_o. \tag{24}$$

Taking into account the ratios of the zone variances at the outlet in units of length ($\sigma_l^2$) and time ($\sigma_t^2$) as well as the average linear rate and velocity of carrier gas at the outlet ($u_o$), we obtain:

$$D_{g,o} = L^2\sigma_t^2 / 2t^3J^3, \tag{25}$$

where $t$ is the exit time of the peak maximum, $J$ is the Martin pressure drop factor.[80] Thus, in order to determine the diffusion coefficients by a continuous elution method in capillary columns at small flow rates there is no need to have an accurate knowledge of the internal diameter of the column. Lochmüller et al.[79] derived an equation that was similar to Eqn. (25) but which did not include the $J$ factor.

According to the law of additive variance of a chromatographic peak, the apparent dispersion is the sum of dispersions inside the column and outside it:

$$\sigma_t^2 = \sigma_{ec}^2 + \sigma_c^2. \tag{26}$$

In turn the extracolumn contribution is the sum of the variances caused by dispersion of the zone at the inlet and in the detector as well as the broadening of the signal in the detector during its amplification and recording.

When two tubes of different length are used, the extracolumn contribution can be excluded by subtracting the variance of the peak obtained on the shorter reference column from the variance of the peak obtained on the main column.[76] Lochmüller et al.[79] determined $D_g$ for argon in helium from a graph of the linear dependence of the apparent variance of the peak on the length of the tubes employed (from 27 to 62 m):

$$\sigma_t^2 = \sigma_{ec}^2 + \frac{2D_{g,o}}{u_0^3}L. \tag{27}$$

When a microkatharometer was used as the detector the value of $\sigma_{ec}^2$ was 35 $s^2$. This method (subtraction of the systematic dispersion of the zone in columns with different length) is also convenient in that as a result only dispersion of the dilute "wings" of the zone are taken into account and hence the potential effect of a high concentration of diffusant in the centre of the zone is eliminated.[79]

In a recent study[81] an attempt was made to compare the 3 methods for the chromatographic determination of diffusion coefficients in a gas: 1) from Eqn. (20) without taking into account the pressure drop; 2) from Eqn. (20) including corrections for the pressure drop in the column (the $J$ correction factor of Martin[80] and $f_g$ correction factor of Giddings[82]

$$D_{g,o} = \frac{L}{4tJ}\left[\frac{H}{f_g} + \sqrt{\left(\frac{H}{f_g}\right)^2 - \frac{d^2}{12}}\right]$$

and 3) by the computer fitting of the van Deemter curve for a nonsorbing compound. In the latter method use was made of a HETP equation which contained, in addition to the usual terms for longitudinal diffusion and resistance to mass transfer in the gas, an additional term that was linearly dependent on the gas velocity. The latter term, according to Bemgard et al.,[81] can result from interphase resistance through friction of the gas against the walls of the CC and nonideal laminarity of its flow. However, according to the calculations of the authors,[81] the contributions from these phenomena do not make up more than 1% of the experimental values of $D_{g,o}$.

The dispersion of $C_4$, $C_6$, and $C_{12}$ n-alkanes and toluene was studied in a quartz capillary column (100 m × 0.32 mm) without a stationary phase in relation to the flow rate of gas ($H_2$, 2–60 cm $s^{-1}$). It was established that the diffusion coefficient values determined by the first two methods depend on the gas velocity and the coefficients calculated when the pressure drop was taken into account increase with the flow rate, while they decrease when the pressure drop is ignored. Extraplation of both dependences to zero flow rate gives the same diffusion coefficient value, which agrees with the value determined by the third method, thus indicating that it is true.

A comparison of the diffusion coefficients determined in this manner with the values predicted by theory from the most accurate Fuller–Schettler–Giddings equation[83] showed that the theory gives overestimated values of $D_g$, which are higher the greater is the length of the n-alkane molecule. Bemgard et al.[81] did not find any correlation between the difference in predicted and experimental values of $D_g$ and the boiling point of the products studied. In this case the geometry of the molecule evidently has a more significant effect on the magnitude of $D_g$, since the above-mentioned equation is based on a solid sphere model and the difference must be greater the more well-defined are the anisotropic properties of the diffusant molecules.

The gas chromatographic determination of the diffusion coefficients of compounds with low volatility presents certain difficulties, mainly because of their adsorption on the inner walls of the tubes. In order to suppress the adsorption sites on the surface of the walls during determination of $D_g$ for polar compounds, trace amounts of these compounds were added to the carrier gas.[84]

In order to determine the diffusion coefficients of heavy n-alkanes, Vasil'ev et al.[85,86] used an even more radical method of deactivating the surface—silanisation of a glass CC with hexamethyldisilazane. There is also some difficulty in introducing the vapour of components with low volatility as a narrow zone into the column. Batched introduction systems that achieve an initial zone width in the capillary columns of the order of 10 or even 1 ms have recently been developed.[87,88] However, when low velocities of carrier gas are used, the width of the chromatographic zone in time units is so great that good results are obtained with the use of a conventional splitter inlet, which is widely used in capillary chromatography.

According to the results of Vasil'ev et al.,[85] extracolumn dispersion when an inlet with divided flow and coventional chromatographic equipment are used is about 0.5 $s^2$. With splitter introduction of the sample and the use of a flame ionisation detector the contribution of extracolumn dispersion was reduced to 0.1% of the peak dispersion and this eliminated the need for its compensation on reference columns.[85,86] When the flow rate of gas was 6—18 mm $s^{-1}$ the pressure drop was negligible and the contribution from resistance to mass transfer was 0.1—0.4%, so these were ignored. Samples of pure alkanes were introduced into the splitter at the minimum level for accurate determination of the peak width to be achieved with maximum sensitivity. In order to include the sight inhibition of zone movement as a result of residual adsorption of heavy alkanes, the factor $(1 + k)^{-2}$, where $k$ is the capacity factor ($0 \leqslant k \leqslant 0.13$), was introduced into Eqn. (25). Using this method, $D_g$ values for $C_5$—$C_{24}$ n-alkanes in helium and n-$C_{18}H_{38}$ and n-$C_{24}H_{50}$ in hydrogen, nitrogen, and argon were determined in silanised glass tubes (1.10 m × 0.25 m and 2.05 m × 0.28 mm).[85,86] It was found that the dependence of the diffusion coefficients of n-alkanes in helium at 200 °C corrected to normal atmospheric pressure on the number of carbon atoms in the molecule ($5 \leqslant n \leqslant 24$) within the limits of experimental accuracy obeyed the equation:

$$D_g^* = 0.081 + 3.553/(n + 1.083). \quad (28)$$

A similar dependence for a more restricted series of n-alkanes ($6 \leqslant n \leqslant 11$) was approximately represented by a linear equation.[89] Although the approximation was carried out on $D_g$ values calculated from the Fuller equation,[83] the deviations of the points from a straight line were hyperbolic in nature, similar to Eqn. (28). The values of $D_g$ calculated from Eqn. (28) for $n = 5$ and 6 were similar to the experimental values for n-pentane and n-hexane determined previously.[84] Indirect evidence for the accuracy of the $D_g$ values determined for alkanes with low volatility may be provided by the good correspondence between the theoretical efficiency calculated from them and the experimental efficiency of the best capillary columns.[86]

### 2. Determination of diffusion coefficients in liquids

Capillary tubes made of stainless steel have generally been used to determine diffusion coefficients in liquids ($D_l$) using the disperson method of Taylor.[90—92] By combining convective dispersion with molecular diffusion in an axial direction, it was possible after a short period of time to obtain considerable dispersion of the zone. The chromatographic equipment used in this method is of simple design and allows for considerable variations in the nature of the diffusant, diffusion medium, and temperature.[93] The reproducibility of the values of $D_l$ obtained by the Taylor method usually constitutes 1—3%.

Alizadeh et al.[94] developed a detailed theoretical basis for use of the Taylor method in determining diffusion coefficients in liquids. Analytical expressions were derived for calculation of corrections to the final volumes of a sample being introduced, recording registers of the detector and connecting tubes, and also corrections to take account of the concentration dependence of $D_l$. It was shown that small changes in the diameter of the column and the eccentricity of its cross-section had virtually no effect on the values of the experimental diffusion coefficients. Subsequently, Wakeham,[95] taking into account the requirements elaborated by Alizadeh et al.,[94] designed a capillary liquid chromatograph in which the error in determination of $D_l$ did not exceed 0.5%.

Evans et al.,[90] by using a steel CC (9.14 m × 0.775 mm), studied the temperature dependence of the diffusion coefficients of spherically symmetric molecules in alcohols. The slope of lines from plots of $\ln D_l$ against $1/T$ were used to determine the activation energies of diffusion; these were 12.6 kJ $mol^{-1}$ in methanol and 23.4 kJ $mol^{-1}$ in octanol. In a later study,[91] in which a CC (61 m × 0.762 mm) was used, an exponential relationship between $D_l$ for spherically symmetric molecules, the viscosity, and temperature was established. Tominaga et al.[92,96] used a column (50.0 m × 0.8 mm) to study temperature dependence of $D_l$ for aromatic compounds in water and established that the dependence of $\ln D_l$ on the reciprocal of the absolute temperature ($1/T$) was curvilinear over a wide temperature range (8—160 °C). The calculated activation energies of diffusion were slightly dependent on the size of the diffusant molecules and decreased almost hyperbolically with an increase in temperature.[96] According to the data obtained, the diffusion coefficients of benzene in water and for self-diffusion of pure water are similar and decrease to an equally marked extent with temperature.

## 3. Determination of diffusion coefficients in supercritical fluids

The diffusion coefficients of compounds in supercritical fluids are approximately equal to the average values of their diffusion coefficients in gases and liquids.[97] A knowledge of diffusion coefficients under near- and super-critical conditions is necessary for supercritical fluid chromatography[98] and in the design of fluid extractors used in the food and pharmaceutical industries.[99]

Flexible quartz CCs without a stationary phase are mainly used to determine diffusion coefficients $D_f$ in fluids. According to the assessment of Springston and Novotny,[97] $D_f$ can be determined to an accuracy of 5% by the Taylor dispersion method. The same authors analysed the possible sources of fixed errors.[97] Thus, it was found that the secondary flow of a fluid MP in coiled columns was insignificant,[98] while the velocity of the MP was sufficiently high for the first component in Eqn. (18) to be neglected.[97] Thus, $D_f$ could be determined from the slope of the mass exchange path of the van Deemter curve for capillary columns without a stationary phase. In the majority of cases the differentials of pressure and density of the fluid phase in the columns were small, and these were neglected.[98,100—104] Extracolumn contributions to dispersion also usually had no effect on the experimental values of $D_f$. In some

cases a variant of the reference column method has been used to take into account the initial dispersion of the zone during introduction.[76] The zone is recorded twice by a UV detector, before and after its passage through the main column. The first detector is placed between a short reference precolumn (1.3–1.8 m) and the main diffusion column of length 46–100 m.[102,104] The compounds are commonly introduced into the columns as solutions in organic solvents, but the dependence of the experimental values of $D_f$ on the nature of the solvent is either only slight[100] or does not occur at all.[97,101,104] Thus, when the fluid phases (propane, $CO_2$) are used as solvents, the experimental diffusion coefficients of phenanthrene are similar to those obtained when solutions of phenanthrene in xylene[105] and methanol in isooctane[101] are used as samples. Adsorption of compounds on the column walls may well result in errors, so asymmetric peaks are not used to calculate $D_f$. It has been noted, however, that adsorption only occurs with low densities of the fluid phases.[97,101]

Springston et al.[97] and Olesik et al.[105] studied the effect of the internal diameter of the column (94–200 μm) and the sample concentrations (15 μg $ml^{-1}$–2.0 mg $ml^{-1}$) on $D_f$ in order to test the reproducibility of the results. The highest reproducibility was achieved with columns of diameter 0.2 mm and samples with a concentration that was close to the investigated upper limit of 2.0 mg $ml^{-1}$. By using a chromatograph that was specially designed for physicochemical measurement under supercritical conditions, whose accuracy in the maintenance of temperature and pressure was ±0.01 °C and ±0.2 atm respectively, the authors of two studies[98,105] reduced the relative standard deviations of the experimental values of $D_f$ to 1–2%. With this precision it was possible to detect a difference between the diffusion coefficients of polyaromatic hydrocarbons and their predeuterated analogues.

The diffusion coefficients of normal and branched symmetric $C_3$–$C_{10}$ ketones, $C_{18}$ fatty acids with a varying degree of unsaturation, liquid crystals, and squalane in fluidised $CO_2$ were determined with the use of a CC (46.23 mm × 0.41 mm). The values of $\ln D_f$ decreased linearly with an increase in density of the mobile phase. The authors established that for isomers or compounds with similar molecular weights, a decrease in the degree of molecular branching and an increase in their rigidity resulted in a decrease in their diffusion coefficients in fluid $CO_2$.[104]

CCs were used to study the temperature dependence of diffusion coefficients in fluids for the systems: benzene–$CO_2$ and methyl linolenate–$CO_2$;[100,103] anthracene–propane and phenanthrene–propane.[98] In all cases with constant densities of the fluid phases (ρ) the values of $\ln D_f$ were inversely proportional to the absolute temperature. From the slope of lines plotted on the coordinates of $\ln D_f$ against $1/T$, calculations were made of the activation energies of diffusion, which were equal to 2.4 and 5.0 kJ $mol^{-1}$ for anthracene and phenanthrene in fluidised propane (ρ = 0.3771 g $ml^{-1}$);[98] 4.52 kJ $mol^{-1}$ for methyl linolenate in $CO_2$ (ρ = 0.8 g $mg^{-1}$);[103] and 4.7 kJ $mol^{-1}$ for napthalene in $CO_2$ (ρ = 0.6 g $ml^{-1}$).[106]

## 4. Determination of diffusion coefficients in polymers

The dispersion method of Taylor is not suitable for determining diffusion coefficients in polymers ($D_p$), since polymers cannot be used as mobile phases because of their high viscosity. However, by depositing polymers as a uniform layer on the inner walls of capillary columns as stationary phases, it is possible to assess their diffusion properties from the resistance to mass transfer in the layers. The resistance to mass transfer ($C_l$) in a uniform layer of liquid phase of thickness $d_f$ is simply related to the diffusion coefficient:

$$C_l = 2d_f^2 / 3D_p. \quad (29)$$

Cramers et al.[107] used this approach to determine $D_p$ for n-alkanes ($C_9$–$C_{20}$) in relatively thick films (1.06–2.35 μm) of polysiloxanes CP-Sil 5 and OV-1 immobilised on the walls of quartz CCs. Three methods for determining the resistance to mass transfer in the SF were tested. The first method was based on a determination of the difference between the experimental HETP and the calculated sum of the contributions from longitudinal and dynamic diffusion in the carrier gas as predicted by the Golay–Giddings equation.[85,108] However, a twofold increase in the thickness of polymer layers resulted in an almost twofold increase in $D_p$ values calculated from Eqn. (29).

Better results were obtained with the second method for determining $C_l$, which was based on the method of "corresponding" velocities[109] corrected for the compressibility of the carrier gas.[110] The efficiency of the columns was determined by using different carrier gases (helium and nitrogen) with velocities proportional to the diffusion coefficients in each of them:

$$\bar{u}_1/\bar{u}_2 = D_{g,1}J_1/D_{g,2}J_2, \quad (30)$$

where $\bar{u}_1$ and $\bar{u}_2$ are the mean linear velocities of the gases, $D_{g,1}$ and $D_{g,2}$ are the diffusion coefficients, $J_1$ and $J_2$ are the Martin[80] pressure drop factors for the first and second carrier gases. The resistance to mass transfer in the stationary phase was defined as the ratio of the differences between the HETPs for each of the gases to the dfference in velocities of the latter:

$$C_l = [(H_1/f_1) - (H_2/f_2)]/(\bar{u}_1 - \bar{u}_2), \quad (31)$$

Here $H_1$ and $H_2$ are the HETPs, $f_1$ and $f_2$ are the Giddings[82] pressure drop factors for the first and second gases. It is clear that this method does not require a knowldge of the absolute values of $D_{g,1}$ and $D_{g,2}$; only their ratio is important, which for may diffusants is the same.[73,111] Cramers et al.[107] calculated the values of $D_{g,1}$ and $D_{g,2}$ from the Fuller equation,[83] which is recognised as the most accurate.[112] Nevertheless, the values of $C_l$ were dependent on the absolute velocities of the gases. In order to eliminate this dependence, a correction to the ratio of the diffusion coefficients in helium and nitrogen was required. The optimum value determined for this (3.16)[107] agreed with the ratio of the experimental values of $D_g$ for octadecane in these gases (3.15).[86]

The third method involved the computer fitting of van Deemter curves. In the opinion of Cramers et al.,[107] this method does not satisfactorily separate the contributions from resistance to mass transfer in the carrier gas and in the stationary phase. This is also supported by the results of Sandra et al.,[113,114] which estimated $D_p$ for n-alkanes and aromatic compounds in thick films of polysiloxanes PS-255 (5 μm) and RSL-300 (3 μm) immobilised on the walls of quartz CCs. Thus, the experimental values of $D_p$ in polyphenylsiloxane RSL-300 for the heavier homologues are higher than for the lighter alkanes whose molecules are, moreover, less bulky.

Pawlisch et al.[58] noted that when resistance to mass transfer in polymer layers predominates in the total dispersion of the zone, the shape of the peak is very sensitive to the diffusivity of the sorbates in them. A twofold decrease in $D_p$ results in marked asymmetry of the form of tailng.

The same authors determined the diffusion coefficients of aromatic compounds in polystyrene (MW 266000) deposited as a uniform thick layer (7–12 μm) in silanised glass CCS, while the

contribution from longitudinal diffusion and resistance to mass transfer in the carrier gas was neglected. Numerical treatment of the computer signals was used to determine the primary and secondary features of the elution curves, and from them the diffusion coefficients in the polymer were calculated. It was established that an increase in temperature from 110 to 140 °C resulted in an increase in $D_p$ values by a factor of $10^2$. The graphs of $\ln D_p$ against $1/T$ were linear. The activation energies of diffusion calculated from the graphs for benzene, toluene, and ethylbenzene were 8.4, 10.0, and 10.6 kJ $mol^{-1}$ respectively. Thus, in view of the possibility of obtaining readily controlled, highly uniform polymer layers, the use of glass capillary columns for studying the diffusion properties of polymers may have considerable future potential.

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