Translated from *Uspekhi Khimii*, 50, 943-972 (1981) U.D.C. 543.544.45

Chromatography in the Gas-Liquid Crystal System

M.S.Vigdergauz, R.V.Vigalok, and G.V.Dmitrieva

The analytical and physicochemical aspects of chromatography using liquid-crystal sorbents are examined and it is concluded that liquid crystals exhibit a unique separating capacity in the analysis of structural isomers. The possibility of using liquid crystals as universal sorbents with a controllable selectivity and suitable for the solution of various analytical problems is demonstrated. The results of the study of the thermodynamics of the sorption of substances by liquid crystals, phase transitions and preceding effects, etc. are presented.
The bibliography includes 178 references.

CONTENTS

I. Introduction 498
II. Analysis of structural isomers 499
III. The use of liquid crystals as stationary phases with a controllable selectivity 502
IV. Chromatographic study of the phase transformations of liquid crystals 508
V. Thermodynamics of the sorption of substances by liquid crystals 509

I. INTRODUCTION

Liquid crystal compounds have been known for about 100 years, but their application in gas chromatography began comparatively recently[1]. The interest in liquid crystals for chromatography is due to the possibility of using them as selective sorbents for the separation of structural isomers, particularly *p*- and *m*-substituted benzenes, whose separation is difficult on the usual isotropic liquids. Reviews have been devoted to the use of liquid crystals in chromatography[2-7]. There is no doubt that *meta*–paraselectivity should be regarded as the principal parameter of the operation of such stationary phases. However, at the present stage of the investigation of the liquid-crystal sorbents it is no longer possible to restrict the treatment to this characteristic. This review deals with problems concerning a more far-reaching study of the sorption properties of mesomorphic compounds in all regions of their phase state, the determination of the position of liquid crystals among other stationary phases, the discovery of the analytical possibilities of liquid-crystal sorbents, the study of phase transitions of the thermodynamics of the dissolution of substances in the isotropic and anisotropic regions, and of the thermal stability of liquid crystals, the investigation of their viscous properties and the associated efficiency of chromatographic columns, the study of mixed phases based on liquid crystals, etc.

The term "liquid crystal" was first introduced by Lehmann[8] for compounds which are characterised, within a certain temperature range, simultaneously by the properties of both liquids (high fluidity, the ability to form drops, etc.) and crystals (optical, magnetic, and electrical anisotropy).

A liquid does not have the three-dimensional order characteristic of a crystal. However, the idea of a liquid as a completely amorphous phase in which the molecules are distributed at random, like the molecules of a gas, is not correct. Studies on the scattering of light and X-rays[9] have shown that there is a short-range order in the arrangement of the molecules in a liquid, i.e. they possess the elements of a crystal structure. The similarity between the liquid and solid states increases when the molecules of the given substance have a planar and extended shape. This favours a more compact packing of the latter and, in the presence of sufficient attraction forces, can lead to the formation of large numbers of molecules oriented in parallel planes. Mesomorphism is observed most often among aromatic compounds. Liquid-crystal compounds containing benzene and naphthalene rings are known. An important group of liquid crystals can be made up of derivatives of cholesterol or compounds with a cyclopentanoperhydrophenanthrene group.

Thus the liquid-crystal state, characteristic of compounds whose molecules have an elongated linear shape with polarisable groups in the structural skeleton, is distinguished by a specific orientation of these molecules in space, involving the arrangement of their longitudinal axes parallel to one another. Liquid crystals are most often formed by compounds whose molecules consist of extended chains incorporating planar aromatic rings with substituents in the *para*-position in the benzene ring; in the presence of substituents in the *ortho*- or *meta*-position, the capacity for the formation of the liquid crystal disappears. An example of a liquid-crystal compound with a single benzene ring is provided by *trans*-*p*-methoxycinnamic acid. The tendency towards mesomorphism increases with increase of the number of connected benzene rings. Groups connecting benzene rings into a chain play a major role. Compounds forming liquid crystals have been described in a series of reviews and monographs[2,3,10-14] and the physical properties and classification of liquid crystals have also been described[2,10,11]. Liquid crystals are much more rarely formed by aliphatic compounds. The explanation is probably the relative flexibility of the long chains in compounds of the paraffinic series.

Liquid crystals can be divided into two main groups. Those in one group are classified as thermotropic liquid crystals; compounds in this class are obtained by heating a solid and exist only in a specific temperature range. Lyotropic liquid crystals constitute the second group and are obtained by mixing two or several components, an amphiphile being usually one of the components. Since only thermotropic liquid crystals are at present used in chromatography, we confine ourselves to the consideration of this class of mesomorphic substances, which include two main types: smectic and nematic; the cholesteric phase is assumed to be a variety of the nematic phase.

When many substances melt, a smectic phase is formed initially in which the molecules are not only arranged parallel to one another but also are fixed in layers; at higher temperatures there is a transition to the nematic phase where this additional order disappears. Cholesteric liquid

crystals are characterised by a helical molecular structure. A single substance has been found containing both nematic and cholesteric phases although individual substances can exist as smectic-nematic or smectic-cholesteric mesophases. The mesophase exists within a specific temperature range characteristic of each substance. When the temperature changes outside the limits of this range, either the usual solid crystal (decrease of temperature) or the isotropic liquid (increase of temperature) is formed.

The most important characteristics of liquid crystals are the melting point involving the transition from the solid state to the mesophase, the point of transition from one mesophase to another, and the clarification point (transition from the liquid-crystal state to the isotropic liquid). Studies have not as yet led to the discovery of a rigorous relation between the structure of the liquid-crystal substance and the type of mesophase, on the one hand, and the selectivity with respect to the *meta*- and *para*-isomers, on the other. Intense investigation of this problem by comparing the experimental results for the variation of molecular structures as well as studies of the influence of a substituent in homologous series led to the discovery of a series of necessary conditions ensuring the maximum steric effect of the mesophase.

II. ANALYSIS OF STRUCTURAL ISOMERS

The first studies of the chromatographic characteristics of liquid crystals already demonstrated their probable usefulness as sorbents for gas chromatography[1,15]. The interaction forces in a sorbate–liquid-crystal melt system, due to the ordered arrangement of molecules in the temperature range of the mesophase, promote the separation of aromatic *meta*- and *para*-isomers with similar boiling points. This effect, first observed by Kelker[1,15] and Dewar and Schroder[16] using *p,p'*-azoxyanisole, proved to be characteristic of many liquid crystals; it is associated with the fact that the more closely linear form of the molecule of the *para*-isomer compared with the *meta*-isomer enables the former to penetrate more readily into the lattice of the liquid crystal and is accordingly more strongly retained by the latter in the temperature range of the mesophase. Above the clarification point, the order of elution of isomers is usually determined by their boiling points[5].

The results of the above investigations led to extensive analytical use of liquid-crystal sorbents[15–71]. The following mixtures have been analysed on columns of liquid crystals: isomeric xylenes[1–6,15–19,22–28,31–44], butylbenzenes[45], vinyltoluenes[46,47], divinylbenzenes[48], mono- and dimethylnaphthalenes[26,46,49], various derivatives of benzene[22,39,41,42], naphthalenes[50–54], and phenol[55], isomers of benefin [*N*-(n-butyl)-*N*-ethyl-2,6-dinitro-α,α,α,-trifluoro-*p*-toluidine] and trifluralin (2,6-dinitro-*N*,*N*-di-n-propyl-α,α,α-trifluoro-*p*-toluidine)[56], isomers of benoxaprofen [2-(4-chlorophenyl)-α-methylbenzoxazole-5-acetic acid][57], terpenes and their derivatives[58], enantiomers of *N*-perfluoroacyl-2-aminoethylbenzene[59,61], steroids[62], heterocyclic aza-compounds[63], polyaromatic hydrocarbons[53,64–66,69–70], cholic acids and α,β-steroid epimers[64, 67,68], and pheromone isomers[71]. At the same time extensive studies have been made on the sorption characteristics of liquid crystals and the thermodynamics of the sorption of different substances by the latter. Studies on these lines have been carried out by Kelker and coworkers[2,17,20,21], Dewar and Schroeder[22,23], Barrall et al.[24], Vigdergauz and coworkers[25–28], Chow and Martire[29,30], etc. Studies have been made on the sorption properties of *p,p'*-azoxyphenetole, a homologue of *p,p'*-azoxyanisole, with a nematic phase existing in the range 138–168 °C, in relation to a large number of paraffinic, naphthenic, and aromatic hydrocarbons[2,15].

A remarkable property of the nematic mesophase of *p,p'*-azoxyphenetole is its high selectivity with respect to positional isomers. Thus the ratio of the retention volumes of *p*- and *m*-xylenes on the above sorbent in the region of the mesophase at 140 °C is $\sigma_H = 1.09–1.10$. Comparison of this quantity with the values obtained[72] for phenanthrene and 7,8-benzoquinoline, used previously for the separation of xylene isomers, indicates a greater selectivity of *p,p'*-azoxyphenetole. Among other aromatic compounds used for the separation of isomeric xylenes, one may mention halogenophthalates, α-naphthylamine ($\sigma_H = 1.089$), 1,8-diaminonaphthalene ($\sigma_H = 1.09$), m-phenylenediamine ($\sigma_H = 1.05$), α,α'-bipyridyl ($\sigma_H = 1.06$), and p-aminoazobenzene ($\sigma_H = 1.05$).[73] These substances proved to be less selective stationary phases than *p,p'*-azoxyphenetole.

The ratios of the retention volumes of the isomeric xylenes (σ_H) on Bentone-34 modified with a silicone oil (in 1:1 proportions) and dinonyl phthalate (60:40) are 1.13 and 1.14 respectively[73]. However, one should point out that Bentone-34 is a technical product consisting of bentonite clay treated with an ammonium base; in particular, Bentone-34 is dimethyloctadecylammonium bentonite. The characteristics of the clay vary from batch to batch, giving rise to difficulties in the exchange reaction with the ammonia base, whence follows the poor reproducibility of the retention characteristics. The non-uniformity of the distribution of isomeric xylenes requires the modification of bentone with a silicone or dinonyl phthalate in appropriate proportions. As a consequence of the non-reproducibility of the results, this ratio also varies from batch to batch. Compared with bentones, liquid crystals have the following advantage: being individual organic compounds and being fairly pure, they ensure the reproducibility of the selective properties and a uniform distribution of isomeric xylenes on the chromatogram[73–76].

The analytical possibilities of *p,p'*-azoxyphenetole have been illustrated in relation to the separation of bicyclic hydrocarbons—mono- and di-methylnaphthalene. The employment of the usual stationary phases, such as cable oil, Apiezon, poly(ethylene glycol)-2000,[77,78] etc. precludes the complete separation of dimethylnaphthalenes as a consequence of the equality of the retention times of 2,6- and 2,7-, 1,3- and 1,6-, and 1,4-, 1,5-, and 2,3-dimethylnaphthalenes. On the other hand, these groups of isomers can be readily separated in the liquid-crystal region of *p,p'*-azoxyphenetole[26]. The retention volumes of alkylnaphthalenes measured in the range 110 to 150 °C indicate their different sorbabilities when the stationary phase passes from the solid to the liquid-crystal state and then to the isotropic liquid state. The elution sequence of alkylnaphthalenes for the solid and isotropic liquid states of the stationary phase is determined by their boiling points and the same dimethylnaphthalene isomers are non-separable as on columns with the usual stationary phases.

The situation is different for the liquid-crystal state of *p,p'*-azoxyphenetole. Here there is a distinct steric effect, which is seen already in relation to monomethylnaphthalenes where the α-isomer is eluted before the β-isomer at 137 °C, although it has a higher boiling point, i.e. the elution sequence is determined by the steric structure of the sorbates. The elution sequence is inverted also in the case of dimethylnaphthalenes. However, one should note that the comparatively low temperature of the analysis, corresponding to the maximum structural selectivity of

azoxyphenetole (137 °C), required a prolonged duration of analysis in the separation of such high-boiling compounds (2.5–3 h). The bisphenetidylterephthalaldehyde liquid crystal used for this purpose is characterised not only by a shorter separation time at 205 °C (down to 15–20 min) but also by a higher selectivity in relation to the isomers indicated[46].

Alkylnaphthalenes were later separated[49] in the nematic and supercooled region of *N,N'*-bis(*p*-methoxybezylidene)-α,α'-bis-*p*-toluidine with a temperature range of the nematic mesophase of 181–320 °C. This liquid crystal is extremely effective also in the separation of benephine from trifluralin[56], the benoxaprofen isomers[57], heterocyclic azacompounds[63], steroids[64,67,68], and polycyclic aromatic compounds[64–66,69–70]. Other examples of the use of the supercooled region of mesophases for the separation of isomers are available in the literature[18,22,24,33,79]. Among the liquid crystals synthesised, mention should be made of the asymmetric azoxyether *p,p'*-ethoxymethoxyazoxybenzene and *p*-methoxybenzylidene-*p'*-butyrylaniline[33,46].

It has been shown[33] that, for a temperature of the analysis close to the melting point of *p,p'*-ethoxymethoxyazoxybenzene, the ratio of the characteristics for *p*- and *m*-xylenes reaches 1.125–1.13, which leads to a significant improvement in the chromatographic separation of the isomers and to a uniform distribution of the peaks of aromatic hydrocarbons on the chromatogram. Isomeric vinyltoluenes have been separated on ethoxymethoxyazoxybenzene[46]. The use of columns with *p*-methoxybenzylidene-*p'*-butyrylaniline permitted the complete separation of aromatic C_8 isomers and isopropylbenzene[46]. It is noteworthy that isopropylbenzene is usually eluted together with *p*-xylene on the liquid-crystal azoxyethers investigated previously.

The elucidation of the influence of the width of the temperature range of the mesophase on the selectivity with respect to positional isomers and of the influence of the nature of the mesophase on the solvent power of the sorbent revealed a relation between these quantities and the *meta–para* selectivity, demonstrating the advantages of compounds with broad regions of the liquid-crystal state. This follows from the data of Kelker et al.[19] (Table 1).

Table 1.

Compound	t_{clar}, °C	t_m, °C	σ_H
4-Methoxybenzylidene-4'-cyanoaniline	117	106	1.03
p,p'-Azoxyanisole (I)	134.5	117	1.04
4-Methoxybenzylidene-4-acetoxyaniline	107	83	1.05
p,p'-Azoxyphenetole (II)	168	13	1.09
60% (I) + 40% (II) eutectic	146	97	1.10

Notation: t_{clar} = clarification temperature, t_m = melting point, and σ_H = selectivity coefficient defined at the ratio of the reduced retention times of the *m*- and *p*-complexes.

The temperature range of the mesophase can be expanded either by synthesising the appropriate liquid-crystal compound or by employing mixed phases forming a eutectic. In the latter case there is a corresponding decrease of the phase transition temperatures together with the expansion of the mesophase region. However, the results of subsequent studies[79,80] showed that the conclusion that the selectivity in relation to isomers varies in parallel with the width of the temperature range of the mesophase is valid only for liquid crystals with similar structures. This is evidently associated with the additional influence of the chemical nature of the sorbent on the selectivity.

This is why the compounds investigated by Kelker[53,81,82], Dewar and Schroeder[16,22], and Vigdergauz and coworkers[80,83] with the width of the temperature range of the nematic mesophase corresponding to 100 and more degrees, exhibit a much lower selectivity in relation to the positional isomers of xylene than *p,p'*-azoxyphenetole. The wide temperature range of the mesophase does not therefore alone guarantee a high selectivity of the sorbent in relation to positional isomers. Nevertheless the synthesis and use of such phases are promising from the analytical standpoint. The retention characteristics of substances on columns with sorbents at high temperatures (above 200 °C) and with broad temperature ranges of the nematic melt have been published[2]. In particular, one can recommend bisphenetidinylterephthalaldehyde (nematic region in the range 198–323 °C), which can be used successfully for the separation of high-boiling components: α- and β-naphthols, α- and γ-benzopyridines, dimethylphthalate, and dimethyl ethers derived from phenanthrene, anthracene, and carbazole, as well as "difficult" pairs of dimethylnaphthalenes[2,19,37,46]. Interesting results have also been obtained on 4,4-bis(benzylidene)benzidine and bis(*p*-methoxybenzylidene)-*trans*-4,4'-diaminostilbene[19].

Liquid-crystal compounds with a nematic mesophase have been most thoroughly investigated. There exist only a few examples of the use of liquid crystals of the smectic and cholesteric type. According to the theory of the liquid-crystal state, the smectic mesophase is characterised by a higher degree of order among the molecules; it therefore appears quite evident that it should exhibit a higher selectivity with respect to positional isomers compared with a nematic melt. However, the opposite behaviour has been most frequently observed in practice and unfortunately the higher order has not been fully realised. The explanation is that the majority of substances are highly viscous in the smectic state, the viscosities sometimes reaching values which cannot be measured on the usual viscometers and the phase transition from the smectic mesophase to the nematic mesophase is measured as the melting point. In this case the smectic region can be observed only by special methods (thermo-optics, thermography, etc.).[84,85]

Naturally the high viscosity of the smectic phase greatly hinders the diffusion of the components analysed for the latter, as a result of which the contribution of adsorption becomes decisive. Two competing factors act in the smectic region: the high degree of order of the molecules leads to the intensification of the *meta–para* selectivity, while viscosity has the opposite effect. Nevertheless one should point out the use of liquid crystal sorbents of the smectic type: ethyl *p,p'*-azoxybenzoate, ethyl *p*-ethoxybenzylideneaminocinnamate, and 4,4'-di-n-hexyloxy- or 4,4'-di-n-heptyloxy-azoxybenzene[15,16,22]. Unusual results have been obtained for a smectic ester, *p*-phenylene bis-*p'*-heptyloxybenzoate, which has a broad region corresponding to the existence of the smectic (79–125 °C) and nematic (125–199 °C) phases[22]. It has been shown that at 68 °C (the solid crystal region) the ratio of the retention parameters of *p*- and *m*-xylenes is 1.10, i.e. corresponds to the experimental structural selectivities of *p,p'*-azoxyphenetole in the eutectic mixture.

Dewar and Schroeder[22,23] noted short retention times of the sorbates and asymmetry of the peaks (the presence of tails) at 68 °C. The elution sequence is *m*- → *o*- → *p*-isomers. The chromatographic characteristics of *p*-phenylene bis-*p'*-heptyloxybenzoate were also examined in other studies[80,83]

in relation to a wide set of paraffinic, naphthenic, and aromatic hydrocarbons in the range 30–220 °C and it was shown that the *meta–para* selectivity of the ester began to be manifested only at 80 °C; this is apparently associated with a decrease of viscosity of sufficient for the contribution of adsorption forces to the retention of sorbates to become significant. The ratio of the retention parameters of *p*- and *m*-xylenes in the smectic region did not exceed 1.03, while in the region of the nematic phase (at 130 °C) it was 1.05.[83]

In the separation of hydrocarbons on *p*-(n-heptyloxy)-benzoic acid[83] an increased solubility of *p*-xylene in both the smectic (92–99 °C) and nematic (99–146.5 °C) mesophases was noted. At 94 °C the ratio of the retention parameters is 1.05 and remains the same at 100 °C (nematic region), i.e. the structural selectivities of both varieties of the mesophase are the same. The much lower selectivity of the acid with respect to the isomers compared with the eutectic mixture of *p,p'*-azoxyanisole and *p,p'*-azoxyphenetole shows that the equality of not only the temperature ranges but also of the absolute melting points and clarification temperatures does not guarantee identical structural selectivities of the sorbents.

An example of the practical utilisation of smectic liquid crystals is provided by the separation of optical isomers carried out by Lochmüller and coworkers[59–61] using optically active mesophases, namely the isopropyl ester of carbonylbis-D-leucine or the alkyl esters of L-valine. However, they showed that the efficiency of separation is in this case determined by chemical reactions, by the intermediate formation of diastereoisomers—hydrogen-bonded association complexes between the stationary phase and the pair of enantiomers. It is known that, apart from liquid crystals, another class of optically active compounds, namely dipeptides, have been used[86,87] for the separation of enantiomers.

The solvent power of cholesteric liquid crystals has been investigated by a number of workers[2,22,24,29,58] as well as Vigdergauz and coworkers[51,88]. A unique property of this mesophase is its high optical activity. In many instances the specific rotation of the plane of polarisation of light is 60000–70000 deg mm^{-1}, while in the case of the usual organic liquids it rarely exceeds 300 deg mm^{-1}. Such a high optical activity is due to the twist in the structure of cholesteric liquid crystals, i.e. a consistent "rotation" of the molecules in their mutual arrangement. It has been suggested that this structure of the mesophase permits the resolution of a racemic mixture into optically active isomers. However, such resolution could not be achieved[2]. Cholesteric liquid crystals did not exhibit an appreciable selectivity with respect to positional isomers either. Nevertheless, one should note that Porcaro and Schubiak[58] used successfully cholesteryl cinnamate together with other smectic and nematic mesophases for the separation of terpene derivatives.

When cholesteryl acetate was used as the stationary phase, the optical isomers of (±)-γ-lactones were separated[89]. The results of studies of the chromatographic characteristics of cholesteryl benzoate (the region of the mesophase is in the range 149–179.5 °C), cholesteryl acetate (94.5–116.5 °C), cholesteryl valerate (93–101.5 °C), and cholesteryl nonanoate (smectic region in the range 77.5–80.5 °C and cholesteric region in the range 80.5–92 °C) in relation to the separation of C_7–C_{10} paraffinic hydrocarbons and aromatic hydrocarbons (benzene, toluene, and ethylbenzene) have also been published[17,24]. The esters investigated exhibited the same features on dissolution of the sorbates as other types of liquid-crystal mesophases, altering the retention characteristics in the case of phase transitions.

The data of Barrall et al.[24], who established a relation between the group selectivity of cholesterol esters in the region of the mesophase and the length of the paraffin chain of the esters, are of interest. Thus, in their isotropic state (120 °C) these cholesterol ester sorbents gave rise to virtually identical retention characteristics of the paraffinic and aromatic hydrocarbons, while in the region of the mesophase the retention of paraffins by cholesteryl nonanoate was much stronger than by other esters. This is apparently a consequence of the interaction of paraffins with long-chain esters, since the retention of aromatic-hydrocarbons is in this case weaker than that of aliphatic hydrocarbons with the same number of carbon atoms in the molecules.

Extensive analytical possibilities arise when mixed sorbents based on liquid crystals are used. Thus, a detailed study has been made[18] of the chromatographic and thermo-optical behaviour of a mixture of cholesteryl benzoate and *p,p'*-azoxyphenetole in relation to the separation of isomeric xylenes. A detailed investigation has been made[88] of the properties of binary sorbents, in the first place those in which one of the ingredients is a liquid-crystal compound [for example, in the separation of dimethylnaphthalenes on compound columns containing *p,p'*-azoxyphenetole and poly(ethylene glycol)-2000; the ratio of the amounts of the stationary phases then corresponds to the ratio of the lengths of the compound column sections indicated] and, in the second place, those in which both ingredients are in the liquid-crystal state. Thus, the authors[88] examined binary mixtures incorporating *p,p'*-azoxyphenetole, *p*-(n-heptyloxy)benzoic acid, the ester of hydroquinone and *p*-(n-heptyloxy)benzoic acid, and cholesteryl cinnamate; the sorbates employed were C_9–C_{11} n-paraffins and *m*- and *p*-xylenes. Deviations were observed from additivity in the retention of sorbates as a function of the composition of the mixed stationary phase. The corresponding deviations are determined both by the energy of the interaction of the components of the stationary phase and by the additional energy of the interaction of the sorbate with the mixture formed.

Eutectic mixtures of nematic mesophases are of greatest interest for chromatography. Studies in this field have been carried out by Kelker[2,19] and the authors of the present review[26,35]. Thus the eutectic mixture *p,p'*-azoxyanisole and *p,p'*-azoxyphenetole in molar proportions of 60:40 was characterised by a high selectivity in the separation of *p*- and *m*-xylenes (the ratio of the reduced retention times was $\sigma_H = 1.11$). Similarly Vigdergauz et al.[26] investigated mixtures of liquid crystals in molar proportions of 20:80, 55:45, 60:35, and 80:20. Andrews et al.[38] studied binary mixtures made up to *p,p'*-dimethoxyazoxybenzene (azoxy-anisole), *p,p'*-diethoxyazoxybenzene (azoxyphenetole), *p,p'*-dibutoxyazoxybenzene, and *p,p'*-dihexyloxyazoxybenzene. The composition of the eutectics of the above liquid crystals was found by recording the phase diagrams. All the eutectics without exception exhibited a much greater structural selectivity than their components. The greatest selectivity was shown by the mixture of *p,p'*-azoxyphenetole and *p,p'*-dibutoxyazoxybenzene (molar ratio 38:62, $\sigma_H = 1.13$). Deviations were then found from additivity in the relation between the retention of the sorbates and the composition of the eutectic. Thus, deviations from the relations governing the variation of the characteristics of the retention of the sorbate by the mixture of *p,p'*-azoxyanisole and *p,p'*-azoxyphenetole, caused by the formation of a eutectic, can be illustrated in relation to s-butylbenzene (Fig.1).

The study of the chromatographic characteristics of binary sorbents with low melting points and a high selectivity in relation to the *meta*- and *para*-isomers are of greater interest[35]. In the preparation of low-melting liquid-crystal mixtures the main component was *p,p'*-ethoxymethoxyazoxybenzene previously recommended for analytical purposes[33], having shown the maximum values $\sigma_H = 1.125-1.13$. The second component consisted of azoxyethers. Binary mixtures based on *p,p'*-ethoxymethoxyazoxybenzene with di-n-hexyloxyazoxybenzene proved to melt at lower temperatures than the main component. Furthermore, it has been shown that the fairly high selectivity, found for the first mixture and equal to 1.115, persists over a comparatively wide temperature range. Thus the use of a binary mixture of liquid crystals as the stationary phase ensures virtually the same selectivity in the separation of *m*- and *p*-xylenes as that of *p,p'*-azoxyphenetole and *p,p'*-ethoxymethoxyazoxybenzene usually employed for these purposes, but at a much lower temperature.

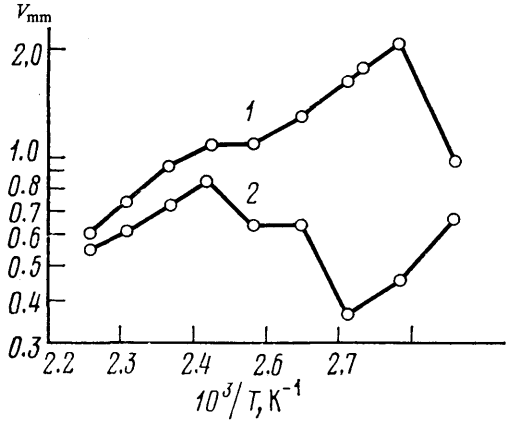


Figure 1. Dependence of the molar retention of s-butylbenzene on the reciprocal of the absolute temperature for a column with a eutectic mixture of *p,p'*-azoxyanisole and *p,p'*-azoxyphenetole[5]: *1*) experimental curve; *2*) curve plotted assuming the additivity of the retention volumes.

III. THE USE OF LIQUID CRYSTALS AS STATIONARY PHASES WITH A CONTROLLABLE SELECTIVITY

Numerous studies in the field of the above liquid crystal stationary phases showed that they are promising as universal sorbents with a controllable selectivity; this is an exceptionally important advance in the application of liquid crystals in gas chromatography in view of the usefulness of such compounds in all regions of their existance: solid, liquid-crystal, and isotropic liquid. Thus, when *p,p'*-azoxyphenetole is used, the chromatographic separation of s-butylbenzene and isobutylbenzene is attained only in the temperature range corresponding to the solid state of the stationary phase[45]. In the separation of cyclohexane and heptane it can also be valuable to ensure conditions corresponding to the solid crystal state of ethoxymethoxyazoxybenzene; the liquid-crystal region is best for the separation of heptane and iso-octane, as well as *m*- and *p*-xylenes, while the isotropic liquid phase of the substance is most selective in the separation of *p*-xylene from isopropylbenzene.

Thus the mesophase should not be regarded as a phase representing a single temperature range suitable for the analytical application of liquid crystals. In the possession of a single column with a liquid-crystal sorbent we have virtually as many stationary phases as the number of states characteristic of the given sorbent. Consequently liquid crystals, behaving as universal stationary phases can, on the one hand, greatly reduce the assortment of general purpose sorbents and, on the other hand, they can be employed for the solution of specific problems.

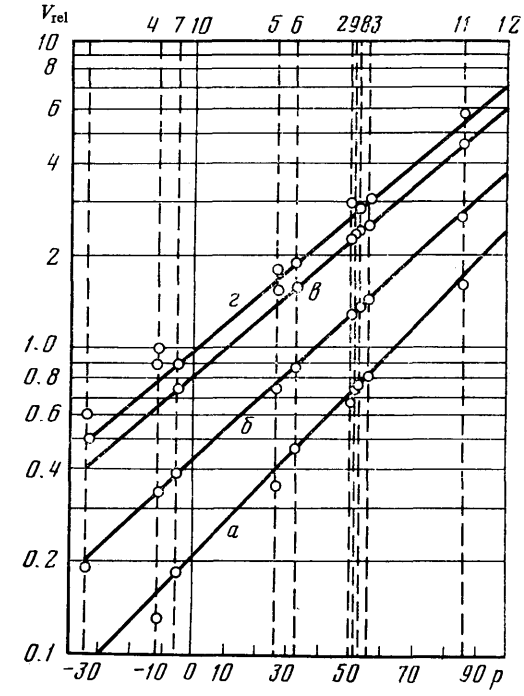


Figure 2. Dependence of the relative retention volumes of alkylbenzenes (on a logarithmic scale) on the conventional polarity of the stationary phases[80]: *1*) eutectic mixture of *p,p'*-azoxyphenetole and *p,p'*-azoxyanisole at 50 °C (SC); *2*) ditto at 100 °C (LC); *3*) ditto at 145 °C (IL); *4*) *p*-(n-heptyloxy)benzoic acid at 50 °C (SC); *5*) ditto at 100 °C (LC); *6*) ditto at 150 °C (IL); *7*) *p,p'*-azoxyphenetole at 110 °C (SC); *8*) ditto at 140 °C (LC); *9*) ditto at 170 °C (IL); *10*) squalane at 140 °C; *11*) poly(ethylene glycol)-2000 at 100 °C; *12*) 1,2,3,4-tetrakis(β-cyanoethoxy)neopentane at 140 °C; sorbates: *a*) benzene; *b*) toluene; *c*) *p*-xylene; *d*) *o*-xylene; notation: SC—solid crystal region; LC—liquid crystal region; IL—isotropic liquid.

1. The Conventional Chromatographic Polarity of Liquid Crystals

In order to estimate the selectivity of liquid-crystal sorbents in different phase states, the conventional chromatographic polarities were determined, by analogy

with Rohrschneider[90], by comparing the retention characteristics of the substances analysed (benzene, toluene, and *p*- and *o*-xylenes relative to n-nonane) on the test and standard sorbents. Fig.2 presents the relations between the logarithms of the relative retention volumes of the sorbates and the conventional chromatographic polarities of the stationary phases. *p,p'*-Azoxyphenetole, *p*-(n-heptyloxy)benzoic acid, cholesteryl cinnamate, squalane, and 1,2,3,4-tetrakis-(β-cyanoethoxy)neopentane were chosen as the stationary phases. Zero polarity was assigned to squalane at 140 °C and 100% polarity was assigned to 1,2,3,4-tetrakis-(β-cyanoethoxy)neopentane at the same temperature. Fig.2 shows that the conventional chromatographic polarity of the liquid crystal varies within wide limits with the phase transitions. In particular, for azoxyphenetole, it increases from -6 (the solid crystal region) to 50 (the anisotropic and isotropic liquid regions).

Thus, whereas in the fused state azoxyphenetole behaves as a moderately polar phase, below the melting point it functions as a non-polar sorbent, ensuring the elution of hydrocarbons virtually in accordance with their boiling points. The conventional chromatographic polarity can vary by 60 units for azoxyphenetole, by 40 units for the acid, and by 25 units for cholesteryl cinnamate. The intermediate values of the conventional chromatographic polarity can be obtained by using a compound column whose sections are filled with the same sorbents but operate at different temperatures. One of the authors of this review attempted to classify the liquid-crystal stationary phases in terms of the general classification based on the Rohrschneider polarity factors by introducing an additional factor *gf* characterising the *meta–para* selectivity of the mesophase[91]. The Rohrschneider equation then assumes the following form:

$$I = I_0 + ax + by + cz + du + es + gf,$$

where *a*, *b*, *c*, *d*, *e*, and *f* are the characteristics of the sorbate and *x*, *y*, *z*, *u*, *s*, and *g* are the characteristics of the sorbent; in particular *g* is the difference between the logarithmic retention indices of *m*- and *p*-xylenes. The following liquid crystals were investigated: *p,p'*-ethoxymethoxyazoxybenzene, *p,p'*-azoxyphenetole, and a binary sorbent consisting of *p,p'*-ethoxymethoxyazoxybenzene and *p,p'*-dibutoxyazoxybenzene[35]. For comparison, data for other stationary phases were also used[76,83,92,93]. It was shown that, in terms of the values of the linear analogues of polarity factors (*X*, *Y*, *Z*, *U*, *S*), the liquid-crystal stationary phases are sorbents of moderate polarity.

In the solution of many practical problems involving the separation of both a group of sorbates and individual positional isomers, it is necessary to select a liquid-crystal stationary phase which possesses fairly high values of the factor *g*, characterising the *meta–para* selectivity of the phase, and of the factor *x*, characterising the conventional chromatographic polarity. In this connection account was taken of the dependence of *g* on *x*, on the basis of which one can select the optimum stationary phase. Fig.3 shows that, although the binary sorbent based on a mixture of dinonyl phthalate and bentone-34 is characterised by a high selectivity in the separation of positional isomers ($g = 16.6$ units of the Kovats index), it is nevertheless a less polar sorbent ($x = 1.25$) than a liquid-crystal phase such as *p,p'*-ethoxymethoxyazoxybenzene ($x = 1.78$ and $g = 15.1$ units of the Kovats index).

The "conventional chromatographic polarity" of a liquid crystal changes abruptly in phase transitions, i.e. on passing from the solid to the liquid-crystal state and then to the isotropic state, increasing as a rule. Within the framework of the same phase state, "the conventional chromatographic polarity" increases with increasing temperature. As regards the *meta–para* selectivity, its magnitude is a maximum at the melting point and then monotonically decreases with increase of temperature. For example, when *p,p'*-azoxyphenetole passes from the solid state (100 °C) to the liquid-crystal state (140 °C), its polarity factor *x* increases from 0.1 to 1.9 units of the Kovats index, while the factor *g*, measured as the difference between the retention indices of *m*- and *p*-xylenes, increases from 2.5 to 14.8 units of the Kovats index. Within the limits of the liquid-crystal state, an increase of temperature from 140° to 150 °C entails a decrease of the *meta–para* selectivity of azoxyphenetole from 14.8 to 12.5 units of the Kovats index.

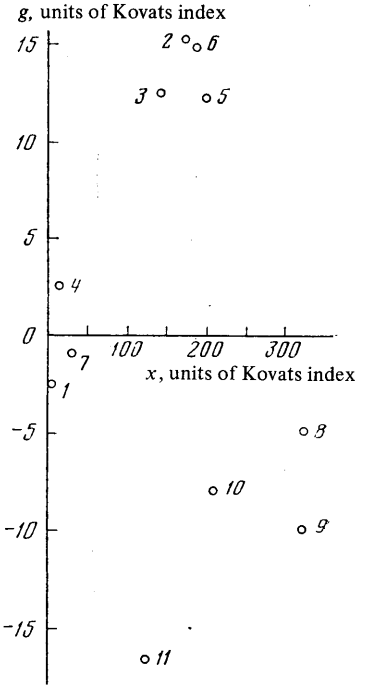


Figure 3. Dependence of the factor *g* on the polarity factor *x*.[91] Stationary phases: *1*) squalane; *2*) *p,p'*-ethoxymethoxyazoxybenzene; *3*) binary phase (*p,p'*-ethoxymethoxyazoxybenzene + *p,p'*-dibutoxyazoxybenzene); *4*) *p,p'*-azoxyphenetole, $t_c = 100$ °C; *5*) *p,p'*-azoxyphenetole, $t_c = 150$ °C; *6*) *p,p'*-azoxyphenetole, $t_c = 140$ °C; *7*) Apiezon L; *8*) PEG-4000; *9*) Rheoplex-400; *10*) Yucon-50NV-2000; *11*) binary phase (dinonyl phthalate + Bentone-34).

Thus the use of the above classification makes it possible to select stationary phases which, together with the extremum values of the factor *g*, have the necessary values of the other polarity factors. According to Herington[94], the selectivity in the separation of sorbates 1 and 2 is characterised by the ratio of their reduced retention times:

$$\sigma_s = t'_{R_2}/t'_{R_1} = (\gamma_1 p_1^0)/(\gamma_2 p_2^0),$$

where p_1^0 and p_2^0 are the vapour pressures of sorbates 1 and 2 and γ_1 and γ_2 are their activity coefficients in solution in the

stationary phase. This polarity index, which we mentioned previously, was used to estimate the *meta–para* selectivities of binary sorbents consisting of *p,p'*-ethoxymethoxyazoxybenzene and di-n-alkoxyazoxybenzenes[35], the influence of the vapour pressures and the activity coefficients of the sorbates (aromatic hydrocarbons–benzene, toluene, ethylbenzene, *o*-, *m*-, and *p*-xylenes) on the separation of the sorbates being estimated.

2. The Influence of Various Factors on the Structural Selectivity of the Liquid-Crystal Stationary Phases

The influence of various factors (temperature, pressure, and sorbate concentration) on the structural selectivity of the mesophase has been examined[95,96]. The temperature dependence of the structural selectivity of liquid-crystal stationary phases has been demonstrated in relation to azoxyethers. The maximum ratio of the retention characteristics of *p*- and *m*-xylenes is observed at the melting point of the liquid crystal and decreases monotonically as the clarification point is approached; above this point, xylenes are eluted as an overall peak. The temperature dependence of the *meta–para* selectivity in the liquid-crystal melt can be accounted for by the analogous dependence of the parameter *S*, which characterises the extent to which the molecules are arranged in parallel[3]; depending on the temperature, the value of *S* for the nematic phase varies in the range from 0.3 to 0.8, but, even at a temperature somewhat below the clarification point, the liquid crystal retains an appreciable tendency towards an ordered mutually parallel arrangement of molecular axes. The transition to the isotropic liquid is accompanied by an abrupt alteration of the sorption characteristics.

Kelker[2] recommends that one should work 2.3 K above the melting point of the substance (the reliability range). However, a detailed examination on the dependence of the retention parameters of the hydrocarbon analysed on temperature showed that there exists a broad region (5–6 K) with the maximum steric effect. Thus the ratio of the retention volumes of *p*- and *m*-xylenes on *p,p'*-azoxyphenetole is 1.096 at 134 °C, 1.10 at 136 °C, and 1.085 at 138 °C. This finding is important, since it shows that the liquid crystals used in gas chromatography do not require any special conditions for the maintenance of the column temperature, so that one can use ordinary commercial chromatographic apparatus. It has been shown that an increase in the concentration of the sorbate and in the carrier gas pressure in the column influence the *meta–para* selectivity in the same direction: the selectivity decreases with increasing concentration of the sorbate and the pressure of the carrier gas, the rate of decrease depending on the nature of both the liquid crystal and the carrier gas. This influence is associated with the breakdown of the ordered structure of the liquid-crystal melt as a consequence of the incorporation of the molecules of extraneous substances.

3. The Viscous Properties of Liquid Crystals

The low viscosity of nematic mesophases such as those of *p,p'*-azoxyanisole, *p,p'*-azoxyphenetole (1.47 cS), their eutectic mixture, and ethoxymethoxyazoxybenzene (3 cS) ensures high efficiency of the operation of chromatographic columns with the above sorbents.

4. Thermal Stability of Liquid Crystals

The use of liquid crystals as sorbents for gas chromatography requires the estimation of their volatility and thermal stability—factors which determine the upper temperature limit of the existence of the stationary phases. The upper temperature limits for the employment of a series of liquid-crystal stationary phases, determined by the derivatographic method, are 180 °C for *p,p'*-azoxyanisole, 200 °C for *p,p'*-azoxyphenetole, 195 °C for the eutectic mixture, 190 °C for *p*-heptyloxybenzoic acid, 270 °C for the ester of hydroquinone and *p*-(n-heptyloxy)benzoic acid, 220 °C for cholesteryl cinnamate, etc.[97,98]. Mention should be made of the work of Dewar and Schroeder[22] specially devoted to the synthesis of thermostable liquid-crystal compounds with high transition temperatures (among 19 new esters – *p*-phenylene alkoxybenzoates, *p,p'*-biphenylene-*p*-alkoxybenzoic acids, or *p*-alkoxycarbonylbenzoic acids - ten had mesomorphic regions extending over more than 90 K and the lowest transition temperature was 205 °C). Kelker et al.[19] studied high-temperature liquid-crystal sorbents. Investigations of the use of bis(*p*-methoxy-. *p*-butoxy-, *p*-hexyloxy-, *p*-phenylbenzylidene)-α,α'-bis-*p*-toluidines for the gas-chromatographic separation of polycyclic compounds[64,66–70] are instructive in this respect.

Naturally in many cases it is useful to carry out the chromatographic analysis at low temperatures, whence follows the necessity for seeking stationary phases in the state of the mesophase in the corresponding temperature range. An example of liquid crystals, with low melting points and clarification temperatures is provided by certain azo-compounds, azoxy-compounds, and azomethines[82,99,100], among which mention may be made of *p*-methoxybenzylidene-*p'*-butylaniline (the temperature range of the mesophase is from 21° to 47 °C), *p*-ethoxybenzylidene-*p'*-butylaniline (from 36 to 80 °C), and their eutectic mixture (from −16° to 50 °C).

Since the vapour pressure is of decisive importance in the estimation of the thermal stabilities of the stationary phases, the study[101] of the temperature variation of the vapour pressure of *p,p'*-azoxyanisole is of interest (Fig. 4).

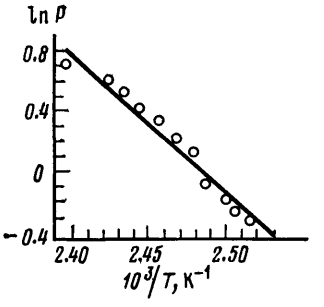


Figure 4. Dependence of the partial vapour pressure (mmHg) on the reciprocal of the absolute temperature[101].

The synthesis of high-temperature crystals holds out extremely great promise, because it extends the region of the analytical applications of mesophases in gas chromatography. Pitch mesophases constitute a fundamentally new type of high-temperature liquid crystals. They can be obtained in two ways: (1) by the carbonisation of coal and

petroleum tars; (2) by the joint carbonisation of individual organic compounds[102–106]. The formation of the liquid-crystal structure in the carbonisation of graphitisable substances is an irreversible process. The pitch mesophase obtained in the range 400–450 °C retains its liquid-crystal structure after complete setting and solidification[102,103]. Thus the temperature range of the existence of the pitch mesophase is much wider than in the other known systems. Brooks and Taylor[102,103] synthesised a series of pitch mesophases based on petroleum products and also by the joint carbonisation of organoelemental compounds and their mixtures (11 specimens); the analytical possibilities of these mesophases were also investigated and their likely usefulness in gas chromatography was demonstrated.

5. Dependence of the Efficiency of a Column with a Liquid Crystal Sorbent on Different Factors

The temperature dependence and the efficiency of a column containing a liquid-crystal sorbent have been studied by many investigators[46,49,79]. It has been shown that the efficiency decreases with decrease of temperature. Thus Fig. 5 presents the temperature variation[46] of the selectivity and efficiency of diundecyloxyazoxybenzene. When the above azoxyether is used for the separation of *m*- and *p*-xylenes at low temperatures, a "favourably" high value of σ_H and an "unfavourably" low value of HETP are obtained. A similar behaviour has been observed[49] in the separation of alkylnaphthalenes on *N*,*N*'-bis(*p*-methoxybenzylidene)-α,α'-bis-*p*-toluidine (BMBT). The authors determined the necessary number (*n*) of theoretical plates in the column for the separation of "difficult" pairs of alkylnaphthalenes on different stationary phases (Table 2).

Table 2.

Stationary phase	Pairs of alkylnaphthalenes*	*n*
Poly(phenyl ether)	1,4- and 2,3-DMN	
	2,3- and 1,5-DMN	85000
p,*p*'-Azoxyphenetole	2,3- and 1,2-DMN	92000
	1,3- and 1,4-DMN	42000
Graphitised thermal black	1,2- and 2,6-DMN	92000
	2,6- and 2,3-DMN	190000
N,*N*'-BMBT	1-EN and 2-MN	6500
	2-EN and 1,3-DMN	6500

*EN and MN = ethyl- and methyl-naphthalenes respectively and DMN = dimethylnaphthalene.

Grushka and Solsky[79,107,108] pointed out different changes in the height equivalent to a theoretical plate *H* as a function of the changes in temperature on a nematic liquid crystal. In particular, using *p*,*p*'-azoxyanisole as the stationary liquid phase on a capillary column[79], they noted the occurrence of temperature hysteresis of *H* (Fig. 6). *H* initially decreases with increasing temperature down to the melting point, where it increases sharply, falls again, and then rises once more in the nematic–isotropic transition. Two different values of *H* were obtained at the same temperature depending on whether the column was heated or cooled, the value of *H* being smaller in the cooling cycle than in the heating cycle. This conclusion is extremely important, since it indicates a high rate of mass transfer to the stationary phase in the cooling cycle (a clear-cut separation of *m*- and *p*-xylenes was in fact achieved in the supercooled region of azoxyanisole on a capillary column at 102 °C).

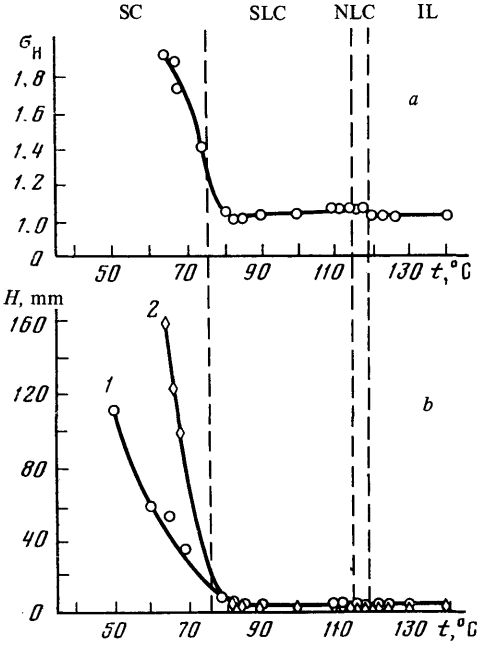


Figure 5. Temperature variation of the selectivity (*a*) and efficiency (*b*) of a column with *p*,*p*'-di-n-undecyloxyazoxybenzene[46]: *1*) *m*-xylene; *2*) *p*-xylene; SLC—smectic liquid crystal region; NLC—nematic region.

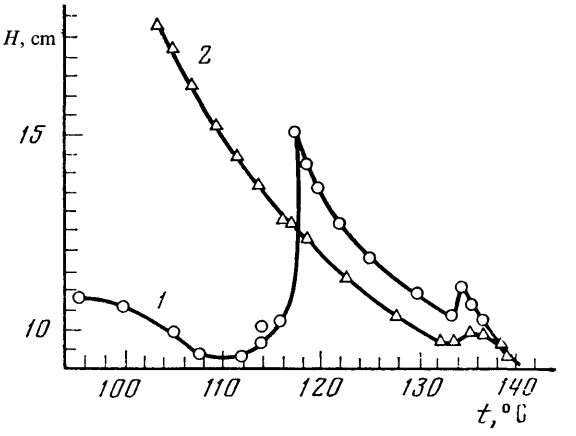


Figure 6. Temperature dependence of the height equivalent to the theoretical plate (HETP):[79] *1*) heating; *2*) cooling.

Grushka and Solsky[79] also showed that the minimum value of *H* is observed for lower flow rates of the carrier gas in the region of the mesophase; for example, in the case of *p*,*p*'-azoxyanisole on a capillary column the minimum value, H_{min}, is attained at a temperature of 120 °C, corresponding to the

liquid-crystal state, while at 90 °C (the solid crystal state of the substance) H_{min} has the same value, but is now obtained at higher carrier gas flow rates. H also decreases with decrease of the amount of stationary phase in the column. On a column with 0.1% of *p*-(*p*-ethoxyphenylazo)phenyl undecylenate (deposited on neutral glass grains), a lower value of H was obtained than on columns containing 0.27 and 0.69% of the stationary phase.

The possibility of the successful use of capillary columns with a liquid-crystal stationary phase has also been demonstrated in a study[40] whose authors used glass capillaries with a length between 8 and 27 m and 0.3 mm in diameter. Treatment of the capillaries with NaOH, NH_3, acids, HF, etc. did not lead to success, and only special treatment with EP-9 epoxy-resin ensured the complete impregnation of the capillary with the liquid crystal and the formation of an effective film. The epoxy-resin mixed with a hardener in proportions of 1:4 was dissolved in *o*-dichlorobenzene and a 10% solution was passed slowly through the capillary with the aid of a water pump. In addition 15 ml of *o*-dichlorobenzene was introduced, after which the capillary was dried at 120 °C in a stream of argon. The liquid-crystal compound was then dissolved in a suitable solvent and was introduced into the capillary by the piston method. The film of the liquid crystal within the capillary was dried in a stream of argon at a slowly rising temperature.

In their study of the retention of sorbate molecules on polymeric sorbents modified with liquid crystals, Zelenkova et al.[109] also showed that the HETP decreases with increase of temperature and with decrease of the amount of the stationary phase. The greatest increase of the sorbent efficiency is observed when 5–20% of the liquid crystal is deposited on the polymeric sorbents.

6. The Influence of the Impregnation of the Carrier

The optimum amount of the stationary phase, deposited on a solid carrier, is determined by the influence of a number of competing factors associated with the selectivity, efficiency, and duration of the analysis. Low degrees of impregnation of the carrier, which make it possible to reduce the HETP and to shorten the duration of the analysis, are preferable. However, in order to obtain exact and reproducible retention parameters (particularly when these are to be used for the calculation of the thermodynamic functions of dissolution), the amount of the stationary phase must be sufficient to achieve the complete coverage of the carrier and to eliminate the distorting influence of adsorption on the surface of the solid.

The influence of the molecular packing density of the test substance on the dependence of the retention parameters on the amount of the stationary phase and also the influence of the solid carrier on the selectivity of the liquid-crystal stationary phase was demonstrated by Gabitova and Vigdergauz[110] for azoxyethers in the separation of *m*- and *p*-xylenes and aromatic and paraffinic compounds using columns with different contents of the stationary phase.

Fig.7 presents the variation of the specific retention volume of toluene on *p,p'*-azoxyphenetole with the degree of impregnation in different phase states. The nature of the curves shows that the contribution of adsorption factors to the retention of sorbates by isotropic and anisotropic liquids is negligibly small for a degree of impregnation exceeding 10%, i.e. above this value the retention parameters are almost independent of the amount of the stationary phase. On the other hand, in the solid crystal state the retention is naturally determined by the area of the adsorbing surface and, since the latter depends only slightly on the amount of the stationary phase, the specific retention volume is inversely proportional to the degree of impregnation V_g. The results permitted the determination of the lower limit of the possible amount of the liquid-crystal stationary phase. They demonstrated a relation between the jump in the retention parameters at the melting point and the degree of their impregnation, while at the clarification point the jump is determined solely by the nature of the substance analysed. Furthermore it has been shown that (1) with decrease in the degree of impregnation the *meta–para* selectivity of the liquid-crystal sorbent diminishes and (2) the temperature of the transition of the stationary phase from the solid state to the liquid-crystal state decreases with decrease in the degree of impregnation.

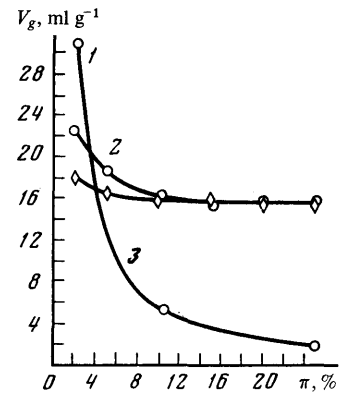


Figure 7. Dependence of the absolute specific retention volume of toluene on the amount of *p,p'*-azoxyphenetole (% relative to the mass of Chromosorb P) at different temperatures (°C): *1*) 100; *2*) 140; *3*) 170.[80]

The principal studies with liquid-crystal sorbents in gas chromatography have been carried out in columns using virtually inert solid carriers which have a specific porosity, are mechanically stable, and have a specific surface of ~10 $m^2 g^{-1}$. The use of liquid crystals deposited in the form of a monolayer on an active solid carrier—macroporous Silochrome with a high specific surface—has been described recently[43,44]. It has been shown that the use of thin, nearly monomolecular layers of nematic and smectic as well as cholesteric stationary phases leads to the observation of a fairly high *meta–para* selectivity and to a shift of the selectivity maximum towards lower temperatures relative to those corresponding to the usual impregnation process (i.e., as in the studies of Serpinet[111,112], a change in the phase transition temperature is observed). Apparently when a monolayer is employed, the support plays an extremely active and possibly a decisive role in the separation of the substances analysed.

The role of an active sorbent with a high surface area in the gas-chromatographic separation of mixtures has been demonstrated by Averin et al.[47], who increased the efficiency of the separation and reduced the temperature of the separation process at high concentrations of the substances analysed by employing an active adsorbent

(Silochrome) impregnated with a liquid-crystal stationary phase (azoxyphenetole) in the separation *m*-, *p*-, and *o*-isomers of vinyltoluene and noted a further series of advantages of this method of separation. In this connection one must also mention studies[109,113] in which polymeric sorbents, such as Polysorb-1 and Chromosorb-101 modified with liquid crystals, for example *p,p'*-azoxyphenetole and *p,p'*-ethoxymethoxyazoxybenzene, were used for the gas-chromatographic separation of various classes of organic compounds—paraffinic and aromatic hydrocarbons, alcohols, ketones, aldehydes, acids, lactones, etc., aromatic compounds being retained on these sorbents more tenaciously than paraffinic hydrocarbons. The separation of *o*- and *m*-xylenes, *o*- and *m*-cresols, etc. has been achieved[109,113], while the *m*- and *p*-isomers were not separated. The influence of the amount of the azoxyphenetole liquid crystal on the principal characteristics of the gas-chromatographic process, on the corrected retention volumes V_R of the sorbates, on the HETP, and on the asymmetry coefficient has been investigated.

The influence of the nature of the solid carrier on the chromatographic behaviour of the mesophase has been noted[79,107,108]. The authors of these investigations suggest that the anomalous effects [the influence of the rate of heating of the liquid crystal on its melting point, the time dependence of the coefficients *K* (the partition coefficient of the sorbate) and the HETP (the efficiency of the separation) near the melting point, the form of the variation of the retention parameters for two ways of varying the temperature in experiments using the capillary column[79] and glass grains of different types[107,108] as the solid carrier] can be explained by the influence of surface orientational forces of the carrier and the inner wall of the capillary tube. Furthermore, it has been shown that the nature of the orienting of the molecules of the liquid crystal on the surface of glass grains is determined by the extent of the diffusion of the sorbate molecules, i.e. the diffusion of solutions in which the molecules of the liquid crystals are oriented parallel to the surface of the glass grains is usually more extensive than the diffusion of solutions with a perpendicular arrangement of liquid crystal molecules on this surface.

The influence of the surface of the solid carrier on the thermodynamic functions of the dissolution of substances has been studied[30,114]. The absence of effects at the solid–liquid crystal interface and the occurrence of only very weak interactions in the gas–liquid crystal system, which can be neglected for a film thickness of at least ~1000 Å, has been demonstrated.

7. The Influence of an Electric Field on the Selective Properties of Liquid Crystals

Under the influence of an electric or magnetic field, the degree of order among the molecules of the liquid crystal changes in the region of the mesophase[115], which leads in its turn to an alteration of the retention characteristics of the substances analysed. In 1963 one of the authors of this review suggested that the chromatographic process be carried out in an electromagnetic field[116]. Under the influence of the field, the molecules of the stationary liquids (and in many instances also the components being separated) are polarised and their sorption properties are therefore altered. Evidently the introduction of an additional factor into the chromatographic process should increase the scope for controlling the selectivity of the stationary phase and permit the study of a new range of sorption phenomena.

The relevant investigations have been carried out by Taylor and coworkers[117–119] using short capillary columns containing mixtures of cinnamate esters and cholesteryl myristate as the stationary phases. An electric field up to 500 V was applied to the column by means of external electrodes attached by means of a special paste and aluminium foil. The authors investigated the dependence of the shape of the peaks and retention times of hydrocarbons and oxygen-containing compounds on the electric potential, its frequency, the analytical temperature and the content of the stationary phase. Application of an electric field increased the retention times of the substances analysed and the peaks became more symmetrical.

Vigdergauz and coworkers[120,121] investigated the influence of an electric field on the chromatographic retention of diethyl ether, acetone, ethyl methyl ketone, n-hexane, heptane, cyclohexane, and benzene, by a liquid-crystal stationary phase—cholesteryl laurate at 86 °C. The length of the spiral column designed by Taylor et al.[117] was 10 m and the potential applied to the electrodes was 500 V. In order to estimate the effect of the electric field, the difference between the free energies of sorption of the test substances $\delta(\Delta F^0)$ in the presence and absence of the field was calculated:

$$\delta(\Delta F^0)\ \text{cal mol}^{-1} = RT \ln \frac{\Gamma'_{500}}{\Gamma'_0} = 714 \ln \frac{\Gamma'_{500}}{\Gamma'_0},$$

where Γ'_{500} and Γ'_0 are the partial Henry coefficients for the sorbates in the presence and absence of the field respectively [$\Gamma' = (t_R/t_0) - 1$, where t_R and t_0 are the retention times of the sorbate and the non-sorbed substance respectively].

The results of the calculation permitted the conclusion that $\delta(\Delta F^0)$ can reach 400–500 cal mol^{-1}, which corresponds, in absolute magnitude, to the value of $\delta(\Delta F^0)$ for the transition from the isotropic liquid to the mesophase[5] and also to the values of $\delta(\Delta F^0)$ for neighbouring homologues, i.e. 100 units of the Kovats index. The use of the above effect for analytical purposes is possible only after the development of a column design ensuring an adequate efficiency. The results justify the hypothesis that, together with familiar external factors such as temperature and pressure, the application of an electric field can also be used for the specific regulation of the selectivity of the chromatographic column.

The following features of the data described above on the analytical application of liquid crystals must be noted:

(1) Despite the fact that extensive studies have been made on the utilisation of liquid-crystal sorbents in gas chromatography, the general characteristics relating the chromatographic selectivity to the structure of the liquid crystal have not so far been discovered[122–124].

(2) The majority of the liquid crystals investigated are designed for the solution of the narrow problem of the separation of *meta*- and *para*-isomers and exhibit a weak group selectivity. Consequently one must direct attention to the synthesis of mesophases exhibiting both specific and general selectivity.

The question arises of the requirements which must be met in the synthesis of liquid-crystal stationary phases:

(a) These must be liquid crystals of the nematic type. The wide-scale employment of smectic liquid crystals will become possible only in the case of very high selectivity. The introduction of new stationary liquid-crystal phases into chromatographic analysis is justified only in those cases where these phases have a significant advantage.

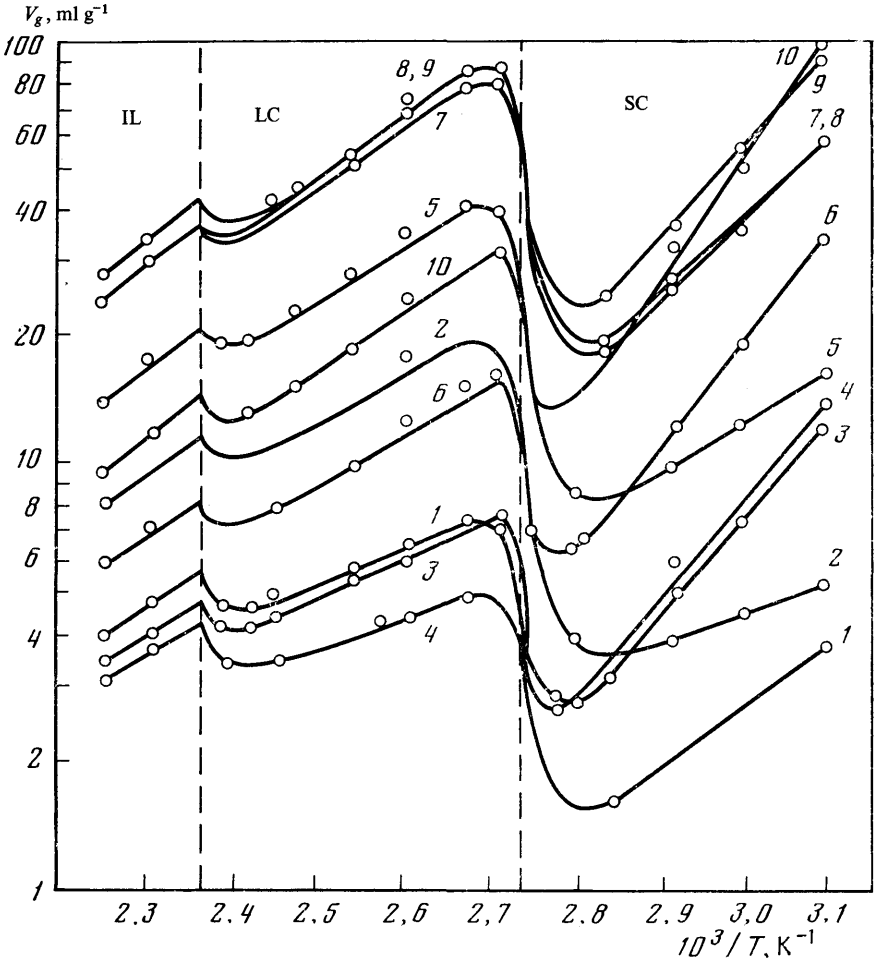


Figure 8. Dependence of the specific retention volumes of hydrocarbons on the reciprocal of the absolute temperature of a column with *p,p'*-ethoxymethoxyazoxybenzene[46]: *1*) cyclohexane; *2*) benzene; *3*) heptane; *4*) iso-octane; *5*) toluene; *6*) octane; *7*) *m*-xylene; *8*) *p*-xylene; *9*) isopropylbenzene; *10*) nonane.

(b) The liquid crystal synthesised must contain highly polar functional groups. Certain examples have been described[125–127], but the analytical scope of such liquid crystals has not so far been estimated. Unfortunately the liquid-crystal stationary phases already investigated are phases of moderate polarity or in practice one has to deal with the separation of a multicomponent mixture consisting of compounds of different classes.

(3) Liquid-crystal stationary phases must have a wide and controllable temperature range of the mesophase. It can be extended either by synthesising the appropriate liquid-crystal compound or by using mixed phases forming a eutectic. The majority of the liquid crystals synthesised are medium-temperature stationary phases the range of the existence of the mesophase of which extends up to 200 to 300 deg. Hence follows the interesting problem of the synthesis and utilisation of the high-temperature phases—the so-called pitch mesophases.

(4) The study of the influence of field effects (electrical and magnetic) on the chromatographic processes in a sorbate–liquid crystal system is of very great interest.

IV. CHROMATOGRAPHIC STUDY OF THE PHASE TRANSFORMATIONS OF LIQUID CRYSTALS

The retention volume and the corresponding retention time (V_R and t_R) in gas chromatography are fundamental characteristics of the sorbate. Fig.8 presents the relations between the logarithm of the specific retention volume and the reciprocal of the absolute temperature of the column containing ethoxymethoxyazoxybenzene[46]. The retention parameters of the substances analysed are extremely sensitive to phase transitions of the sorbent as a consequence of which the plot clearly reveals three regions of its phase state: solid, liquid-crystal, and isotropic liquid. The phase transitions are accompanied by sharp changes in the retention parameters. Under these conditions, the retention volumes increase at the melting point by a factor of 4–10 and at the clarification temperature by 15–20%. The melting point, clarification temperature, and transition temperature between different mesophases are characterised by an abrupt alteration of the retention parameters; on the other hand, there are cases where

there is no maximum, for example, when *p*-phenylene bis-*p'*-(n-heptyloxy)benzoate passes from the solid state to the smectic mesophase, which is due to the high viscosity of the latter[5,83].

Within the framework of the same temperature range between the phase transition temperatures, there is a gradual decrease of the retention volumes as the temperature rises. The transition from the solid to the liquid-crystal state leads to a change of the overall selectivity, which is expressed by an inversion of the elution sequence of aromatic, naphthenic, and paraffinic hydrocarbons. The same relations determining the temperature variation of the retention were observed by Kelker[15] for *p,p'*-azoxyphenetole, by Dewar and Schroeder[16] for *p,p'*-di-n-hexyloxyazoxybenzene, and by Barrall et al.[24] for cholesteric liquid crystals. In particular, Barrall et al.[24] noted that the elution times of the sorbates increase by a factor greater than 3.5 on transition from the cholesteric mesophase to the isotropic liquid.

Further studies demonstrated that there is a more complex relation between the retention and temperature. Thus, when the solid-crystal phase of ethoxymethoxyazoxybenzene is heated[33] and its isotropic liquid phase is cooled in the range 70–100 °C, hysteresis is observed, i.e. the retention of the sorbates and the selectivity of their separation are linked to the "memory" of the column. Other workers have also observed hysteresis[49,79].

The high sensitivity of the sorption characteristics and the associated retention parameters of the substances analysed to the phase state of the sorbent permits the solution also of the converse problem—the determination of the phase transition temperatures and also of the accompanying structural changes with the aid of chromatographic apparatus. This advanced gas chromatography to the forefront of the effective methods for the investigation of physicochemical properties and phase transformations in liquid crystals[24]. The likely usefulness of the combined study of phase transitions in liquid crystals by thermography and a combination of gas chromatography and the thermo-optical method was first demonstrated by Vigalok and coworkers[46,85].

Fig. 9 presents the thermo-optical curve for the dependence of the logarithm of the retention of hydrocarbons on the reciprocal of the temperature of the column with *p,p'*-heptyloxyazoxybenzene and a thermogram of this substance. The graphical data demonstrate the full agreement within the limits of 1–2 K of the phase transition temperatures determined by all three methods: sorption, optical, and thermal, despite the fact that the principle of each is different. As regards the additional information which can be obtained with the aid of chromatography, one should note the possibility of the study of the prefusion process and the accompanying structural changes in the crystal as well as a quantitative estimate of these changes (Kelker[20] pointed out earlier the occurrence of prefusion effects in liquid crystals which were treated by various investigators either as homogeneous processes or as processes involving heterogeneous fluctuations[128,129]).

Using a combination of the chromatographic and thermo-optical methods, the phase transitions in binary liquid-crystal sorbents have also been determined. It has been shown that the greatest shift of the phase transition temperature towards low values, amounting to 30 K, has been observed for the eutectic mixture of *p,p'*-ethoxymethoxyazoxybenzene and di-n-butoxyazoxybenzene, while the corresponding shift for the mixture with di-n-hexyloxyazoxybenzene amounts to 18 K.[35] The phase transition temperatures can also be determined by differential scanning calorimetry combined with gas–liquid chromatography (GLC).[30]

The idea of nematic order in poly(vinyl chloride) has been confirmed by chromatographic studies[130]. It has been shown that the nature of the separation of the *cis*- and *trans*-decalins differs markedly in the experimental temperature range (35–170 °C) and that the elution sequence of the isomers undergoes inversion as a function of the phase state of the sorbent.

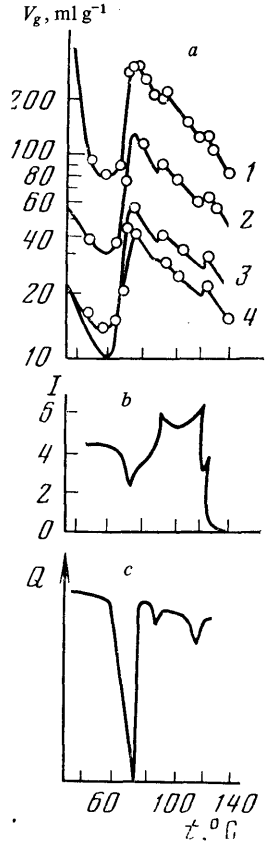


Figure 9. Chromatographic (*a*), thermo-optical (*b*), and thermographic (*c*) curves for *p,p'*-heptyloxyazoxybenzene[46]. Sorbates: *1*) *p*-xylene; *2*) toluene; *3*) n-pentane; *4*) benzene.

V. THERMODYNAMICS OF THE SORPTION OF SUBSTANCES BY LIQUID CRYSTALS

The possibility of the analytical and preparative separation of compounds with similar boiling points by chromatography in a gas–liquid crystal system is due to the significant differences between the thermodynamic functions of the sorption of isomeric compounds by liquid crystals. Gas chromatography is therefore an effective method for the investigation of the properties of the solvent and the behaviour of the solute in the liquid crystal, as well as the determination of the thermodynamic parameters of mesophases; one can then determine from chromatographic data the thermodynamic parameters under conditions close to infinite dilution, where no disruption of the structure of the liquid-crystal phase is observed[29,30,48,114,131–136]. Furthermore, the absence of an influence on the accuracy of the

determination of the thermodynamic parameters by effects on the solid–liquid crystal and gas–liquid crystal interfaces for a thickness of the liquid crystal film of ~1000 Å was noted above.

On the basis of the analysis of the activity coefficients γ^{∞} of the sorbates at infinite dilution, a molecular theory of the solubility of substances in liquid crystals has been developed[135]. The activity coefficients have been interpreted at the molecular level by means of statistical mechanics. As usual, the thermodynamic calculations are based on the determination of the specific retention volume V_g.

In their study of the effects of the dissolution of xylenes in cholesteryl myristate, which can exist in the state of both smectic and cholesteric mesophases, Martire et al.[29] established that only the smectic phase gives rise to the selective separation of *m*- and *p*-xylenes. Kelker[18] also pointed out the absence of selectivity in the cholesteric phase, while Vetrova and coworkers[43,44] achieved a fairly clear-cut separation of *m*- and *p*-xylenes on cholesteryl pelargonate deposited in a monolayer on an active adsorbent. Unfortunately, the authors of the present review were unable to reproduce these results.

Jeknavorian and coworkers[139,140] derived the same relations for the solubilities of the above compounds in liquid-crystal sorbents as Chow and Martire[135] on the basis of an analysis of the activity coefficients for the dissolution of n-alkanes and aromatic hydrocarbons, including xylenes and *cis*- and *trans*-isomeric alkyl cyclohexyl ethers on the *p*-(*p'*-ethoxyphenylazo)phenyl heptanoate nematic liquid crystal.

The phase transition temperatures are known to be preceded by pretransformation periods. Kelker and coworkers[20,21] showed that the effects preceding the phase transitions can be investigated by chromatographic methods; azoxyethers (azoxyanisole, azoxyphenetole, and their eutectic mixtures) can be investigated by chromatographic methods. Prefusion processes have been described[128,129]. Pretransition effects have also been demonstrated by measurements of viscosities[141], specific heats[142], coefficients of linear expansion of NMR signals[143], and infrared spectra[144]. Bauer and Bernamont[145] found in relation to *p,p'*-azoxyanisole that the pretransformation period occurred ~10 K below the clarification temperature. To account for the pretransition effects, Kelker used the molecular-statistical theory developed by Tsvetkov[146], Weber[143], and Maier and Saupe[147]. The pretransition behaviour of nematic phases can be described also with the aid of the Frenkel's two-phase concept[148].

The thermodynamics of the dissolution of substances in liquid crystals has been studied[42] by capillary gas chromatography. On the basis of the molecular theory of solubility[135], the authors investigated the influence of the length of the alkyl chains in the homologous series of liquid-crystal ketoximes on the molar enthalpy Δh^0 and entropy Δs^0 of the solution and the excess functions of the dissolution of the above substances.

It has been shown[42] that the partial molar enthalpies and entropies of all the sorbates (alkanes, aromatic hydrocarbons, xylenes, and disubstituted benzenes) exhibit a clear alternation in the homogous series of ketoximes with inversion at the clarification temperature. Compounds with an even number of carbon atoms had lower values of Δh^0 and Δs^0 at a higher clarification temperature. The disubstituted benzene isomers used as sorbates were fully separated and the *p*-isomers exhibited higher values of Δh^0 and lower values of γ^{∞} in the region of nematic liquid crystals.

The thermodynamic functions of the sorption of different sorbates on liquid crystals have been studied by Vigdergauz and coworkers[5,26,83,85,88]. Calculations showed that the transition from the anisotropic to the isotropic region is accompanied by an increase of the heat of sorption and that, whereas in the isotropic region the values of Δh for the isomers are similar, in the case of the mesophase there are significant differences due to the molecular structure of the sorbates.

Kelker showed for alkylbenzenes[15] that the heat of mixing of xylenes with *p,p'*-azoxyphenetole is an order of magnitude higher than the heat of mixing with the usual stationary liquids. Thus, the heats of mixing of *o*-xylene with the azoxyphenetole mesophase, benzylbiphenyl, and 7,8-benzoquinoline are 5400, only 520, and 850 cal mol^{-1} respectively. The heat of mixing is always higher by ~3000 cal mol^{-1} in the mesophase than in the isotropic liquid; consequently the dissolution process in an anisotropic composition requires more energy, i.e. the dissolution of substances in both the liquid-crystal and isotropic regions of the sorbent is accompanied by the adsorption of heat and the mesophase is more endothermic in all instances apart from the eutectic mixture.

The corresponding difference for *p,p'*-azoxyphenetole[83,85] amounts to 2–3 kcal mol^{-1}, which agrees with the data of Kelker[15], who, however, used in the calculation the latent heats of vaporisation λ at the boiling points of the sorbates and not at the column temperature. The change in the degree of endothermicity on transition from the isotropic liquid to the mesophase decreases for *p*-(n-heptyloxy)-benzoic acid, the ester of hydroquinone and *p*-(n-heptyloxy)-benzoic acid, and cholesteryl cinnamate to 0.5–1 kcal mol^{-1}, while in the case of the eutectic mixture the corresponding difference for paraffins is close to zero and for the remaining alkylbenzenes and cycloparaffins it amounts to ~1 kcal mol^{-1}.

Comparison of the heats of sorption and the excess enthalpies of mixing with those observed in the case of the isotropic phase and the mesophases (smectic and nematic) of the ester of hydroquinone and heptyloxybenzoic acid showed that the smectic region is the most endothermic: $\Delta h \cong 4$ kcal mol^{-1} (in the nematic region $\Delta h = 1.2$–2.3 kcal mol^{-1}) The results can be accounted for by the higher degree of order in the structure of the smectic region, so that the penetration of extraneous molecules into the mesophase of the smectic liquid crystal requires a greater expenditure of energy than in the case of the nematic state. For anisotropic melts of azoxyphenetole, the entropy of mixing Δs is greater by 8–10 e.u. than for the isotropic phase.

Thus the transition of the sorbent to the liquid crystal region is accompanied by a sharp change of both the entropy of mixing of the sorbate with the stationary liquid (which corresponds to an abrupt alteration of the retention characteristics in the temperature range of the phase transition) and of the enthalpy of mixing (which corresponds to a dependence of the logarithms of the retention characteristics on $1/T$). The set of these changes ensures extensive possibilities for the regulation of the selectivity in the separation of mixtures incorporating isomers with similar boiling points.

As already mentioned, a considerable scope for the regulation of selectivity arises from the use of mixed stationary phases[5,26,35,88]. The nature of the intermolecular interaction in such a system depends on whether the binary system includes one or two liquid-crystal compounds, on whether they form a eutectic mixture, and on the type of mesophase of the mixed liquid-crystal ingredients. It is noteworthy that the absolute difference between the heats of sorption of the substances analysed in the isotropic and anisotropic regions on the individual sorbents is greater than on the mesophase. This effect had been noted earlier by Kelker[2] in relation to o-xylene

and shows that the mixing process is accompanied by a change in the energy of the system. The excess free energy of the mixed phase $\Delta f'$ can be calculated on the basis of published data[149,150] from the formula

$$\lg V_{mm} = x_1 \lg V_{mm1} + (1-x_1) \cdot \lg V_{mm2} + \Delta f'/4.57T,$$

where $V_{mm} = V_g M/22400$ is the molar retention, x_1 the mole fraction of the individual phase in the mixture, T the column temperature (K), and M the molecular weight of the stationary phase.

For the sorbates investigated, the above relation is represented by curves with a maximum corresponding to the 60:40 eutectic mixture; the maximum value of $\Delta f'$, calculated from the dependence of the molar retention on the phase composition, then corresponds to 100 °C, i.e. a temperature close to that of eutectic fusion (Fig.10). The effective value of Δf, obtained for a 10% degree of impregnation of Chromosorb on the basis of the retention characteristics of n-paraffins, proved to be 630–640 cal mol^{-1}. The value of $\Delta f'$ calculated from the retention characteristics of polar compounds are significantly greater, since they include the energy of the specific interaction of the sorbate with the eutectic.

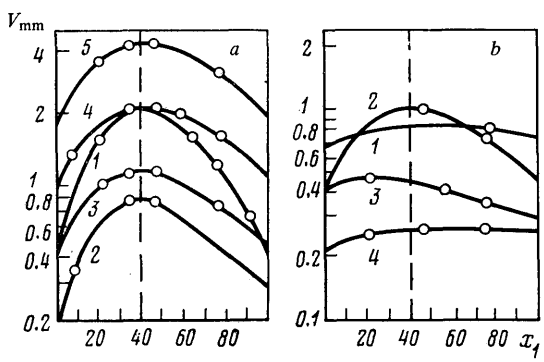


Figure 10. Dependence of the molar retention of sorbates (on the logarithmic scale) on the content of p,p'-azoxyphenetole x_1 in its mixture with p,p'-azoxyanisole[5]. The dashed lines correspond to the eutectic mixture: *a*) retention of s-butylbenzene (curve *1*), butyl acetate (curve *2*), n-decane (curve *3*), n-undecane (curve *4*), and n-dodecane (curve *5*) at 100 °C; *b*) retention of n-decane at different temperatures (°C); *1*) 90; *2*) 100; *3*) 140; *4*) 170.

The excess free energies of mixing of the individual components $\Delta f'$ (from the data for n-paraffins) as well as the values of $\Delta f'$ characterising the additional energy of the interaction of xylenes with binary solvents were calculated for binary systems incorporating p,p'-azoxyphenetole (I), p-(n-heptyloxy)benzoic acid (II), p-phenylene bis-p'-(n-heptyloxy)benzoate (III), cholesteryl cinnamate (IV), poly(ethylene glycol)-2000 (V), and squalane (VI).[5,88]

In the first place the determination of the dependence of $\Delta f'$ and $\Delta f''$ on the composition of mixtures of p,p'-azoxyphenetole with poly(ethylene glycol) and squalane permitted the conclusion that the values of the calculated functions are determined by the phase state of the liquid-crystal ingredient. Thus, whereas at temperatures of 170° and 190 °C corresponding to the isotropic liquid state the values of $\Delta f'$ are virtually the same (Table 3)[88], transition to the temperature at which the mesophase exists (140 °C) entails an increase of $\Delta f'$ by 400 cal mol^{-1}. A negative value of $\Delta f''$ for xylenes has been observed in the case of the p,p'-azoxyphenetole–squalane pair, which is characterised solely by the dispersion interaction between the components.

Table 3. Experimental values of $\Delta f = \Delta f' + \Delta f''$ (cal mol^{-1}) for binary systems of phases[88].

Sorbates	(I)–(V) 140° C	(I)–(V) 170° C	(I)–(V) 190° C	(I)–(VI) 140° C	(I)–(II) 136° C	(II)–(III) 100° C	(III)–(IV) 156° C
n-Paraffins	560	150	140	770	270	520	—160
m-Xylene	730	310	300	450	260	800	—120
p-Xylene	320	320	320	400	260	830	—110

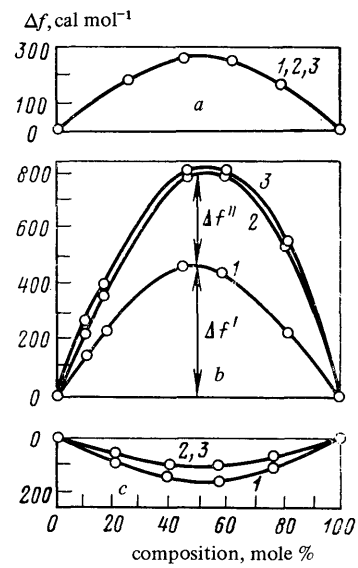


Figure 11. Dependence of the quantity $\Delta f = \Delta f' + \Delta f''$ on the composition of a binary liquid crystal phase[88]. Systems: *a*) (I)–(II); *b*) (II)–(III); *c*) (III)–(IV). Sorbates: *1*) n-paraffins ($\Delta f'$); *2*) *m*-xylene; *3*) *p*-xylene.

The values of $\Delta f'$ for the liquid-crystal mixtures (I)–(II) and (II)–(III) are positive, while those for the (III)–(IV) mixture are negative. One cannot rule out the possibility that the latter is associated with the transition of the entire (III)–(IV) system to the state of a cholesteric mesophase (by analogy with Friedel's data[151]). Fig.11 presents relations between Δf and the composition of a binary liquid-crystal phase. Evidently in the (I)–(II) system the curves corresponding to n-paraffins and xylenes coincide. This indicates an additive variation of the selectivity in the separation of xylenes as a function of the composition of the phase and the absence of additional specific interactions ($\Delta f'' = 0$). The coincidence of the curves corresponding to

xylenes in the (III)–(IV) system is a consequence of the virtual absence of selectivity in both components of the mixed phase at the temperature of the measurement. In the (II)–(III) system an anomalous increase of selectivity is observed with a maximum corresponding to an ether content of 10 mole %. This composition of the mixed phase yields a ratio of the retention volumes of *p*- and *m*-xylenes of 1.065–1.070, while for the individual phases (II) and (III) the ratios are respectively 1.05 and 1.02.

* * *

During the period when the manuscript was with the editors, a number of studies devoted to various theoretical and applied aspects of chromatography in the gas–liquid crystal system were published. The separation of structural isomers of various substituted dialkylbenzenes has been achieved[152–159] on columns with mesophases containing azo- and azoxy-groups. The isomeric dimethylnaphthalenes have been analysed[160–162] and polycyclic aromatic hydrocarbons, in particular anthracene, phenanthrene, benzo phenanthrene, benzopyrenes, and perylene have been investigated[160–165]. Substances of biological origin—cholic acids and their derivatives, steroids, and phenolic metabolites of benzo[*a*]pyrene—have been investigated with the aid of high-temperature nematic liquid-crystal phases[166,167]. In addition enzymes have been analysed[168] and enantiomeric *N*-pentafluoropropionamides have been separated on smectic mesophases[169]. Problems of the influence of the solid carrier on the chromatographic characteristics of liquid-crystal stationary phases have been studied[154,160,170–172] and a number of investigations have been devoted to the thermodynamics of the dissolution of sorbates in mesophases[173–176].

The study of the influence of an electric field on the separating capacity of liquid crystals has been continued[177] and capillary columns have been used[164,178].

REFERENCES

1. H.Kelker, Ber.Bunsenges,Phys.Chem., **67**, 698 (1963).
2. H.Kelker and E.Schivizhoffen, Adv.Chromatog., **6**, 247 (1968).
3. G.H.Brown, Anal.Chem., **41**, 26 (1969).
4. I.Illy, Anal.Chem., **29**, 216 (1974).
5. M.S.Vigdergauz and R.V.Vigalok, "Uspekhi Gazovoi Khromatografii" (Advances in Gas Chromatography), Kazan, 1975, No.4, p.27.
6. H.Kelker, "Advances in Liquid Crystals", Acad. Press, New York–San Francisco–London, 1978, Vol.3, p.237.
7. Z.Witkiewicz, Wiad Chem., 1, 19 (1977).
8. O.Lehmann, Z.phys.Chem., **5**, 427 (1890).
9. P.Debye, Z.Elektrochem., **45**, 174 (1939).
10. G.H.Brown and W.G.Shaw, Chem.Rev., **57**, 1049 (1957).
11. V.A.Usol'tseva and I.G.Chistyakov, Uspekhi Khim., **32**, 1124 (1963)[Russ.Chem.Rev., No.9 (1963)].
12. D.Vorlander, Ber., **41**, 2033 (1908).
13. G.W.Gray, "Molecular Structure and the Properties of Liquid Crystals", Acad.Press, London–New York, 1962.
14. I.G.Chistyakov, "Zhidkie Kristally" (Liquid Crystals), Izd.Nauka, Moscow, 1966.
15. H.Kelker, Z.analyt.Chem., **198**, 254 (1963).
16. M.J.S.Dewar and J.P.Schroeder, J.Amer.Chem.Soc., **86**, 5235 (1964).
17. H.Kelker, "Gas-Chromatographie 1965. Vorträge des V Symposiums", Berlin, 1965, p.271.
18. H.Kelker and H.Winterscheidt, Z.analyt.Chem., **220**, 1 (1966).
19. H.Kelker, B.Scheurle, and H.Winterscheidt, Analyt.Chim.Acta, **38**, 17 (1967).
20. H.Kelker and A.Verhelst, J.Chromatog.Sci., **7**, 30 (1969).
21. H.Kelker, J.Chromatog., **112**, 165 (1975).
22. M.J.S.Dewar and J.P.Schroeder, J.Org.Chem., **30**, 2296, 3485 (1965).
23. M.J.S.Dewar, J.P.Schroeder, and D.C.Schroeder, J.Org.Chem., **32**, 1692 (1967).
24. E.M.Barrall, P.S.Porter, and J.F.Johnson, J.Chromatog., **21**, 392 (1966).
25. R.V.Vigalok, A.M.Tsibulevskii, and M.S.Vigdergauz, "Neftepererabotka i Neftekhimiya. Spetsial'nyi Vypusk Posvyashchennyi XI Mezhdunarodnomu Gazovomu Kongressu, 1970" (Petroleum Processing and Petrochemistry. Special Issue Devoted to the XIth International Gas Congress, 1970), p.12.
26. M.S.Vigdergauz and R.V.Vigalok, Neftekhimiya, **11**, 141 (1971).
27. R.V.Vigalok, A.M.Tsybulevskii, and M.S.Vigdergauz, Neftepererabotka i Neftekhimiya, No.3, 17 (1972).
28. R.V.Vigalok, G.G.Maidachenko, G.A.Seichasova, I.F.Khatypov, N.A.Palikhov, R.K.Nasybullina, and M.S.Vigdergauz, "III Vsesoyuznaya Konferentsiya po Zhidkim Kristallam. Tezisy Dokladov" (The IIIrd All-Union Conference on Liquid Crystals. Abstracts of Reports), Ivanovo, 1974, p.197.
29. D.E.Martire, P.A.Blasco, P.F.Carone, L.C.Chow, and H.Vicini, J.Phys.Chem., **72**, 3489 (1968).
30. L.C.Chow and D.E.Martire, J.Phys.Chem., **73**, 1127 (1969).
31. H.Kelker, Abh.Dtsch.Acad.Wiss.Berlin, Kl.Chem., Geol.Biol., **49** (1966).
32. A.Ono, Nippon Kagaku Kaishi, **4**, 811 (1972).
33. R.V.Vigalok, N.A.Palikhov, G.A.Seichasova, G.G.Maidachenko, and M.S.Vigdergauz, in "Uspekhi Gazovoi Khromatografii" (Advances in Gas Chromatography), Kazan, 1973, No.3, p.34.
34. G.G.Maidachenko, R.V.Vigalok, and M.S.Vigdergauz, USSR P. 455 276 (1974); Byul.Izobret., No.48 (1974).
35. R.V.Vigalok, R.K.Gabitova, N.P.Anoshina, N.A.Palikhov, G.G.Maidachenko, and M.S.Vigdergauz, Zhur.Anal.Khim., **31**, 644 (1976).
36. M.S.Vigdergauz and R.V.Vigalok, Vestnik Akad. Nauk SSSR, No.10, 73 (1977).
37. "Zhidkie Kristally—Unikal'nye Sorbenty dlya Gazovoi Khromatografii" (Liquid Crystals—Unique Sorbents for Gas Chromatography), Advertising Leaflet, Kazan, 1973.
38. M.A.Andrews, D.C.Schroeder, and J.P.Schoeder, J.Chromatog., **71**, 233 (1972).
39. A.B.Richmond, J.Chromatog.Sci., **9**, 571 (1971).
40. G.Kraus, K.H.Seifert, and H.Schubert, Z.Chem., **11**, 428 (1971).
41. G.Kraus, K.H.Seifert, and H.Schubert, Z.Chem., **11**, 22 (1971).
42. G.Kraus, K.H.Seifert, and H.Schubert, J.Chromatog., **100**, 101 (1974).
43. Z.P.Vetrova, D.A.Vjakhirev, N.T.Karabanov, G.G.Maidachenko, and J.I.Jashin, Chromatographia, **8**, 643 (1975).
44. Z.P.Vetrova, N.T.Karabanov, and J.I.Jashin, J.Chromatog., **10**, 341 (1977).

45. M.S.Vigdergauz and R.V.Vigalok, "Materialy Nauchnoi Konferentsii IOFKh, Kazan, 1970" (Proceedings of the Scientific Conference of the Institute of Physical and Organic Chemistry, Kazan), 1970, p.166.
46. R.V.Vigalok, G.G.Maidachenko, G.A.Seichasova, R.K.Nasybullina, T.R.Bankovskaya, N.A.Palikhov, and M.S.Vigdergauz, in "Uspekhi Gazovoi Khromatografii" (Advances in Gas Chromatography), Kazan, 1975, No.4, p.115.
47. V.A.Averin, V.Ya.Shnol', and A.P.Domarev, USSR P.501350 (1976); Byul.Izobret., No.4 (1976).
48. W.L.Zielinski, D.H.Freeman, D.E.Martire, and L.C.Chow, Anal.Chem., **42**, 176 (1970).
49. S.Wasik and S.Chesler, J.Chromatog., **122**, 451 (1976).
50. G.Chiavari, Atti Accad.Naz.Lincei., Cl.Sci.Fis., Mat.Nat., Ser.VIII, **51**, 531 (1971).
51. G.Chiavari and L.Pastorelli, Chromatographia, **7**, 30 (1974).
52. G.Chiavari, A.Arcelli, A.M.Di Pietra, Atti Accad. Naz.Lincei., Cl.Sci.Fis., Mat.Nat., Ser.VIII, **52**, 381 (1972).
53. H.Kelker, B.Scheurle, J.Sabel, J.Jainz, and H.Winterscheidt, Mol.Cryst.Liq.Cryst., **12**, 113 (1971).
54. V.A.Chernysheva and M.S.Vigdergauz, Zhur. Anal.Khim., **32**, 1176 (1977).
55. L.E.Cook and R.C.Spangelo, Anal.Chem., **46**, 122 (1974).
56. M.Hall and D.H.B.Mallen, J.Chromatog.Sci., **14**, 451 (1976).
57. M.Hall and D.H.B.Mallen, J.Chromatog., **118**, 268 (1976).
58. P.I.Porcaro and P.Schubiak, J.Chromatog.Sci., **9**, 690 (1971).
59. C.H.Lochmüller and R.W.Souber, J.Chromatog., **87**, 243 (1973).
60. C.H.Lochmüller and R.W.Souber, J.Chromatog., **88**, 41 (1974).
61. C.H.Lochmüller and R.W.Souber, J.Chromatog., **113**, 283 (1975).
62. D.N.Kirk and P.M.Shaw, J.Chem.Soc.C, 3979 (1971).
63. M.Pailer and V.Hlozek, J.Chromatog., **128**, 163 (1976).
64. G.M.Janini, K.Johnston, and W.L.Zielinski, Anal. Chem., **47**, 670 (1975).
65. Chromatographia, **11**, 593 (1976).
66. G.M.Janini, G.M.Muschik, and W.L.Zielinski, Anal. Chem., **48**, 809 (1976).
67. G.M.Janini, G.M.Muschik, W.Manning, and W.L.Zielinski, in "Abstr.Pittsburgh Conf.Anal. Chem.and Appl.Spectrosc.Cleveland, Ohio, 1977", Pittsburgh Pa, 1977, p.360.
68. W.L.Zielinski, L.Walter, K.Johnston, and G.M.Muschik, Anal.Chem., **48**, 907 (1976).
69. G.M.Janini, G.M.Muschik, J.A.Schoer, and W.L.Zielinski, Anal.Chem., **48**, 1879 (1976).
70. G.M.Janini, B.Shaikh, and W.L.Zielinski, J.Chromatog., **132**, 136 (1977).
71. R.Lester, J.Chromatog., **156**, 55 (1978).
72. S.H.Langer and J.H.Purnell, J.Chem.Phys., **67**, 263 (1963).
73. M.S.Vigdergauz and O.G.Chabrova, Neftekhimiya, **4**, 932 (1964).
74. M.S.Vigdergauz, L.V.Andreev, and O.G.**Chabrova**, Zhur.Anal.Khim., 22, 265 (1967).
75. M.S.Wigdergaus, L.W.Andrejew, M.I.Afanasiew, and O.G.Tschabrowa, "Gas-Chromatographie, 1965. Vorträge der V Symposiums", Berlin, 1965.
76. M.S.Vigdergauz and O.G.Chabrova, Neftekhimiya, **5**, 160 (1965).
77. I.A.Musaev, Ch'i-Wei Ku, A.V.Topchiev, and P.I.Sanin, Neftekhimiya, **1**, 459 (1961).
78. J.A.Walker and D.L.Ahlberg, Anal.Chem., **35**, 2028 (1963).
79. E.Grushka and J.F.Solsky, Anal.Chem., **45**, 1836 (1973).
80. R.V.Vigalok and M.S.Vigdergauz, Izv.Akad.Nauk SSSR, Ser.Khim., 715 (1972).
81. H.Kelker, B.Scheurle, R.Hatz, and W.Bartsch, Angew.Chem., **82**, 984 (1970).
82. H.Kelker and B.Scheurle, Angew.Chem., **81**, 903 (1969).
83. R.V.Vigalok, Candidate's Thesis in Chemical Sciences, All-Union Petrochemical Research Institute (VNIINEFTEKhIM), Leningrad, 1971, 132 pp.
84. B.Ya.Teitel'baum and N.A.Palikhov, Vysokomol. Soed., **10**, 468 (1968).
85. R.V.Vigalok, N.A.Palikhov, and M.S.Vigdergauz, Kristallografiya, **17**, 837 (1973).
86. E.Gil-AV and B.Feibush, Tetrahedron Letters, 3345 (1967).
87. J.Corbin and L.B.Rogers, Anal.Chem., **42**, 974 (1970).
88. R.V.Vigalok and M.S.Vigdergauz, Izv.Akad.Nauk SSSR, Ser.Khim., 718 (1972).
89. P.Molina and A.Soler, J.Cambronero, An.Quim., **71**, 629 (1975).
90. L.Rohrschneider, Z.analyt.Chem., **170**, 256 (1959).
91. M.S.Vigdergauz, R.K.Gabitova, R.V.Vigalok, and I.R.Novikova, Zavod.Lab., **45**, 894 (1979).
92. J.Bonastre and P.Grenier, Bull.Soc.chim.France, 1395 (1967).
93. M.S.Vigdergauz, "Gazovaya Khromatografiya kak Metod Issledovaniya Nefti" (Gas Chromatography as a Method for the Investigation of Petroleum), Izd. Nauka, Moscow, 1973, p.221.
94. E.F.G.Herington, "Vapour Phase Chromatography" (Edited by D.H.Desti), Butterworths, London, 1957, p.5.
95. R.Kh.Mar'yakhin, V.A.Ezrets, R.V.Vigalok, and M.S.Vigdergauz, in "Uspekhi Gazovoi Khromatografii" (Advances in Gas Chromatography), Kazan, 1973, No.3, p.43.
96. V.A.Ezrets and M.S.Vigdergauz, "Vsesoyuznaya Konferentsiya po Fiziko-Khimicheskomu i Preparativnomu Primeneniya Khromatografii" (All-Union Conference on the Physicochemical and Preparative Applications of Chromatography), Izd.Zinatne, Riga, 1976, p.13.
97. V.A.Byl'ev, L.A.Polyakova, and M.S.Vigdergauz, Zavod.Lab., **35**, 908 (1969).
98. V.A.Byl'ev, L.A.Polyakova, and M.S.Vigdergauz, in "Uspekhi Gazovoi Khromatografii" (Advances in Gas Chromatography), Kazan, 1970, No.2, p.115.
99. H.Kelker and B.Scheurle, Angew.Chem., **24**, 24 (1970).
100. R.Steinsträsser and L.Pohl, Z.Naturforsch., **26b**, 577 (1971).
101. J.F.Solsky and E.Grushka, J.Phys.Chem., **78**, 275 (1974).
102. **J.D.**Brooks and G.H.Taylor, Carbon, **3**, 185 (1965).
103. **J.D.**Brooks and G.H.Taylor, Nature, **206**, 697 (1965).

104. K.J.Hüttinger, Bitumen, Teere, Peche, Asphalte und verwandte Stoffe, **21**, 487, 528 (1970).
105. K.J.Hüttinger, Ber.Dtsch.Keram.Ges., **48**, 216 (1971).
106. H.March, Fuel, **52**, 205 (1973).
107. E.Grushka and J.F.Solsky, J.Chromatog., **99**, 135 (1974).
108. E.Grushka and J.F.Solsky, J.Chromatog., **112**, 145 (1975).
109. N.F.Zelenkova, L.I.Panina, and K.I.Sakodynskii, in "Novye Sorbenty dlya Gazovoi Khromatografii" (New Sorbents for Gas Chromatography), NIITEKhIM, Moscow, 1978, p.52.
110. R.K.Gabitova and M.S.Vigdergauz, Zhur.Anal.Khim., **51**, 1205 (1977).
111. J.Serpinet, J.Chromatog., **68**, 9 (1972).
112. J.Serpinet, J.Chromatog., **77**, 289 (1972).
113. N.F.Zelenkova, L.I,Panina, and K.I.Sakodynskii, in "Analiticheskie Primeneniya Khromatograficheskikh Protsessov" (Analytical Applications of Chromatographic Processes), NIITEKhIM, Moscow, 1976.
114. J.M.Schur and D.E.Martire, Anal.Chem., **43**, 1201 (1971).
115. I.G.Chistyakov, Kristallografiya, **5**, 962 (1960).
116. M.S.Vigdergauz and V.A.Ezrets, in "Uspekhi Gazovoi Khromatografii" (Advances in Gas Chromatrography), Kazan, 1979, No.5, p.77.
117. P.J.Taylor, R.A.Culp, C.H.Lochmüller, L.B.Rogers, and E.M.Barrell, Sep.Sci., **6**, 841 (1971).
118. P.J.Taylor, A.O.Ntukogu, S.S.Metcalf, and L.B.Rogers, Sep.Sci., **8**, 245 (1973).
119. J.E.Conaway and L.B.Rogers, Sep.Sci., **13**, 303 (1978).
120. V.A.Ezrets, A.V.Garusov, and M.S.Vigdergauz, Zhur.Fiz.Khim., **52**, 2702 (1978)[Russ.J.Phys.Chem., No.10 (1978)].
121. V.A.Ezrets, A.V.Garusov, and M.S.Vigdergauz, "Vsesoyuznaya Konferentsiya po Fiziko-Khimicheskomu i Preparativnomu Primeneniya Khromatografii" (All-Union Conference on the Physicochemical and Preparative Applications of Chromatography), Izd.Zinatne, Riga, 1976, p.65.
122. W.Ecknig, H.Kreigsmann, and H.Rotzsche, Ber.Bunsenges Phys.Chem., **76**, 587 (1967).
123. G.Kraus and A.Kolbe, J.Chromatog., **147**, 17 (1978).
124. N.Kotsev and D.Shopov, Dokl.Bolg.Akad.Nauk, **21**, 889 (1968).
125. "II Vsesoyuznaya Konferentsiya po Zhidkim Kristallam i Simpozium po Ikh Prakticheskomu Primeneniya. Tezisy Dokladov" (The IInd All-Union Conference on Liquid Crystals and the Symposium on Their Practical Applications. Abstracts of Reports), Ivanovo, 1972.
126. "III Vsesoyuznaya Konferentsiya po Zhidkim Kristallam i Ikh Prakticheskomu Ispol'zovaniyu. Tezisy Dokladov" (The IIIrd All-Union Conference on Liquid Crystals and Their Practical Applications. Abstracts of Reports), Ivanovo, 1974.
127. "IV Vsesoyuznaya Konferentsiya po Zhidkim Kristallam i Ikh Prakticheskomu Ispol'zovaniyu. Tezisy Dokladov" (The IVth All-Union Conference on Liquid Crystals and Their Practical Applications. Abstracts of Reports), Ivanovo, 1977.
128. A.R.Ubbelohde, "Melting and Crystal Structure" (Translated into Russian), Izd.Mir, Moscow, 1969.
129. V.N.Tsvetkov and E.I.Ryumtsev, Kristallografiya, **13**, 290 (1968).
130. S.A.Liebmann, D.H.Ahlstrom, and C.R.Foltz, J.Chromatog., **67**, 153 (1972).
131. D.G.Willey and G.H.Brown, J.Phys.Chem., **76**, 99 (1972).
132. D.E.Martire and L.Z.Pollara, Adv.Chromatog., **1**, 335 (1965).
133. L.C.Chow and D.E.Martire, Mol.Cryst.Liq.Cryst., **14**, 293 (1971).
134. L.C.Chow and D.E.Martire, "Liquid Crystals" (Edited by G.H.Brown and M.M.Labes), 1973, Vol.3, p.937.
135. L.C.Chow and D.E.Martire, J.Phys.Chem., **5**, 2005 (1971).
136. D.G.Willey and D.E.Martire, ACS Symposium, Abstr.No.121, New York, 1971.
137. H.T.Peteson, D.E.Martire, and W.Lindner, J.Phys. Chem., **76**, 596 (1972).
138. D.G.Willey and D.E.Martire, Mol.Cryst.Liq.Cryst., **18**, 55 (1972).
139. A.A.Jeknovorian and E.F.Barry, J.Chromatog., **101**, 299 (1974).
140. A.A.Jeknovorian, P.Barrett, A.C.Waterson, and E.F.Barry, J.Chromatog., **107**, 317 (1975).
141. R.S.Porter and J.F.Johnson, J.Appl.Phys., **34**, 51 (1963).
142. H.Arnold and H.Sackmann, Z.phys.Chem., **213**, 137 (1959).
143. K.H.Weber, Discuss.Faraday Soc., **25**, 7 (1958).
144. W.Maier and G.Englert, Z.Elektrochem., **64**, 689 (1960).
145. E.Bauer and I.Bernamont, J.Phys.Radium, **7**, 19 (1936).
146. V.N.Zwetkoff, Acta Physicochim.USSR, **16**, 132 (1942).
147. W.Maier and A.Saupe, Z.Naturforsch., **15a**, 287 (1960).
148. Y.Frenkel, J.Chem.Phys., **7**, 538 (1939).
149. W.Kemula, H.Buchowski, and J.Terepek, Bull.Acad. Polon.Sci.Ser.Sci.Chim., **9**, 595 (1961).
150. A.Waksmundzki and Z.Suprunowicz, J.Chromatog., **188**, 232 (1965).
151. G.Friedel, Ann.phys., **18**, 273 (1922).
152. Z.Witkiewicz, Z.Suprynowicz, J.Wojcik, and R.Dambrowski, J.Chromatog., **152**, 323 (1978).
153. Z.Witkiewicz and S.Popiel, J.Chromatog., **154**, 60 (1978).
154. Z.Witkiewicz, M.Pietrzyk, and R.Dąbrowski, J.Chromatog., **177**, 189 (1979).
155. Lu Peichang and Li Haochun, J.Chromatog., **184**, 215 (1980).
156. K.P.Naikwadi, D.G.Panse, V.Bapat, and B.B.Ghatge, J.Chromatog., **195**, 309 (1980).
157. F.Vernon and A.N.Khakoo, J.Chromatog., **157**, 412 (1978).
158. K.Hitoshi and S.Yoshihito, Bunseki Kakagu, **28**, 92 (1979).
159. A.Ono, J.Chromatog., **180**, 170 (1979).
160. Z.Witkiewicz and A.Waclawczyk, J.Chromatog., **173**, 43 (1979).
161. K.Tesarik, J.Frycka, and Z.Ghyczy, J.Chromatog., **148**, 223 (1978).
162. V.Hlozek and H.Gutwillinger, Chromatographia, **13**, 234 (1980).
163. G.M.Janini, K.Johnston, and W.L.Zielinski, Jr., in "29th Pittsburgh Conf.State Art and Anal.Chem. and Appl.Spectrosc., Cleveland, Ohio, 1978. Abstracts", Monroeville, Pa, p.426.
164. W.L.Zielinski and G.M.Janini, J.Chromatog., **186**, 237 (1979).
165. F.Janssen, Anal.Chem., **51**, 2163 (1979).

166. G.M.Janini, W.B.Mannirg, W.L.Zielinski, and G.M.Muschik, J.Chromatog., **193**, 444 (1980).
167. W.L.Zielinski, G.M.Janini, C.M.Mischik, R.I.Sato, M.M.Miller, R.M.Young, D.M.Jerina, D.Thakker, H.Yagi, and W.Levin, "29th Pittsburgh Conf.State Art.Anal.Chem.and Appl.Spectrosc., Cleveland, Ohio, 1978. Abstracts", Monroeville, Pa, p.210.
168. R.Lester and D.R.Hall, J.Chromatog., **190**, 35 (1980).
169. C.H.Lochmüller and J.V.Hinshaw, J.Chromatog., **171**, 407 (1979).
170. S.Popiel and Z.Witkiewicz, Bull.WAT J.Dabrowskiego, **27**, 29 (1978).
171. Z.Witkiewicz, Z.Suprynowicz, and R.Dabrowski, J.Chromatog., **175**, 37 (1979).
172. J.Rayss, Z.Witkiewicz, A.Waksmundzki, and R.Dabroski, J.Chromatog., **188**, 107 (1980).
173. M.Isamu and H.Kishimoto, J.Pharm.Soc.Japan, **98**, 689 (1978).
174. D.E.Martire, A.Nikolic, and K.L.Vasanth, J.Chromatog., **178**, 401 (1979).
175. J.F.Bocquet and C.Pommier, J.Chromatog., **117**, 315 (1976); **166**, 357 (1978).
176. A.Radicki, H.Lamparczyk, and R.Kaliszan, Chromatographia, **12**, 595 (1979).
177. K.Wababe, S.Suzuku, and S.Araki, J.Chromatog., **192**, 89 (1980).
178. K.Seifert and G.Kraus, J.Chromatog., **192**, 97 (1980).

Arbuzov Institute of Physical and Organic Chemistry, Kazan