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LIQUID-CRYSTALLINE STATIONARY PHASES FOR GAS CHROMATOGRAPHY

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I. INTRODUCTION

Gas chromatography is of great importance in modern chemical analysis and physico-chemical investigations, as can be seen from the wealth of publications on the subject¹. It is to be expected that the role of gas chromatography will not diminish for a long time despite the rapid development and increasing role played by liquid chromatography. The possibilities afforded by gas chromatography have not been as yet fully utilized, and much remains to be achieved by applying apparatus and columns with new designs. It seems, however, that the greatest expectations should be attached to the column fillings. Today many types of fillings for adsorption and partition chromatography are known. Most of them, especially in the case of liquid stationary phases, have very similar properties, and increasing their number serves no purpose. It seems promising, however, to seek stationary phases that differ distinctly from those known so far and have new, advantageous properties. Among such stationary phases for partition chromatography are liquid crystals.

The history of research on and applications of liquid crystals, referred to by Kelker as "beautiful substances", is extremely interesting. Discovered at the end of the 19th century, they were initially merely a scientific curiosity, and it was only after many years that they found a wide range of applications. The use of liquid crystals as stationary phases in gas chromatography was described for the first time in 1963. Since then, liquid-crystalline stationary phases have been applied successfully to separations of composite mixtures, chiefly isomers, including those of polycyclic hydrocarbons.

2. GENERAL PROPERTIES AND STRUCTURE OF LIQUID CRYSTALS

Liquid crystals represent a specific state of matter intermediate between a crystalline solid and an isotropic liquid. A substance in the liquid-crystalline state is a liquid and shows mechanical properties specific to liquids, but at the same time shows some anisotropic properties of a solid crystal, the latter being due to the preservation of a degree of ordering higher than in liquids.

Thermo- and lyotropic liquid crystals can be distinguished. In thermotropic crystals, the liquid-crystalline state is established after the solid is melted. The resulting liquid preserves, in a certain temperature range, properties intermediate between those of the solid and the liquid, but upon further heating a transition takes place at a given temperature, called the clearing temperature, to the isotropic liquid. The temperature difference between the melting point and the clearing temperature determines the mesophase range. Lyotropic liquid crystals show liquid-crystalline properties over a wide range of concentrations in a suitable solvent. They are obtained by mixing two or more components. Usually they are solutions of surface-active agents or polymers. In gas chromatography so far only thermotropic liquid crystals have been used. It seems, however, that certain lyotropic systems could also find applications in gas chromatography, for instance in the form of mixed phases.

Depending on the way the molecules are ordered, *i.e.*, on their structure, thermotropic liquid crystals are classified into nematic, cholesteric and smectic types. According to some classifications the cholesteric liquid crystals are treated as a specific case of nematic liquid crystals. Diagrams showing the ordering of molecules in liquid-crystalline systems are presented in Fig. 1.

In nematics the molecules are arranged approximately parallel along their long axes (Fig. 1a). The molecules are not perfectly parallel owing to their thermal movement. As a result, the orientation of the long axes is, in the absence of external forces, variable. The degree of parallelity or ordering of the molecules is determined by the parameter S , the value of which varies from zero for molecules arranged at random to unity for molecules ordered ideally. For nematics S assumes values from 0.3 to 0.8. Nematic liquids can be oriented by a magnetic or electric field or by the substrate. The substrate can orient the long axes of liquid crystal molecules horizontally or vertically to its surface. Any intermediate orientation of the molecules is also possible.

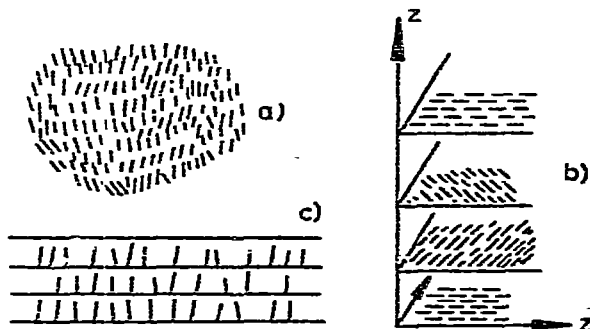


Fig. 1. Diagrams of liquid-crystalline structures: (a) nematic; (b) cholesteric; (c) smectic.

The cholesteric structure is a twisted nematic structure (Fig. 1b), which occurs in compounds with chiral molecules or in mixtures including a chiral compound. The values of S are the same as in nematics.

In the smectic structure the molecules are arranged parallel to each other in layers (Fig. 1c). In smectic liquid crystals S has values greater than 0.8. Eight types of smectic structures are distinguished, denoted by A, B, C, D, E, F, G and H.

After melting, the liquid crystal can assume one of the above structures and preserve it in the whole mesophase range or assume a more ordered smectic structure and subsequently, at a higher temperature, transform into a nematic or cholesteric phase. The phase transitions connected with the change of structure in liquid crystals can be of either the first or second kind.

There are two theories for the interpretation of the liquid-crystalline state. One is the domain theory, in which the lack of clearness of the liquid-crystalline phase is due to the existence of anisotropic domains of ordered molecules of dimensions corresponding to the wavelength of visible light. In the domains we observe ordering characteristic of the given liquid-crystalline structure. In one domain there are usually about 10^5 molecules. The domains themselves have a random orientation. The lifetime of a domain is limited and the molecules can pass from it to the isotropic surrounding or to another domain.

However, the domain theory does not explain all of the phenomena observed in liquid crystals, so a newer elastic continuum theory was advanced which assumes that all sites in a liquid crystal have a preferred orientation in the direction of the long axes of the molecules. It has been found that in many instances explanations of the same phenomenon in terms of both theories give similar results. This is, among other things, the reason why the domain theory, which additionally is more demonstrative, is also used today.

The molecules of liquid crystals are usually elongated and rigid and generally have polar terminal groups. Liquid crystals are encountered in many groups of organic compounds, including Schiff bases, azo and azoxy compounds and esters. Most known liquid crystals have been summarized by Demus and Zschke². In view of their optical, electrooptical and thermo-optical properties, liquid crystals have found application, e.g., as displays and temperature meters. Detailed information on the properties of liquid crystals can be found in several books³⁻⁵.

3. PROPERTIES OF LIQUID CRYSTALS SIGNIFICANT FOR GAS CHROMATOGRAPHY

With most conventional (especially non-polar) stationary phases, separation of mixtures takes place due to differences in the boiling temperatures of the particular components. There are, however, many substances (e.g., isomers) that have identical or very similar boiling temperatures, so that their separation on those phases is very difficult or impossible. Such substances differ, however, as regards their molecular structure and liquid-crystalline stationary phases are well suited for their separation.

When considering the structure of liquid crystals, it has been found that they should have different properties as solvents compared with conventional isotropic liquids. It has been shown that the use of liquid crystals as solvents provides new possibilities of investigating various compounds by NMR, IR, ESR and UV methods

and that the liquid crystals have a specific effect on chemical reactions proceeding^{3,5,10}. It was therefore expected that liquid crystals would be good stationary phases for separating geometric and optical isomers.

The first work, by Kelker^{11,12}, and later by Dewar and Schroeder^{13,14}, was very promising and prompted studies on liquid-crystalline stationary phases. Several surveys have already been published devoted as a whole or in part to certain aspects of applying liquid crystals in gas chromatography^{3,15-28}. Mention is also made of liquid-crystalline stationary phases in textbooks on gas chromatography^{29,30}.

So far more than 200 works have been published, many in recent years, describing the properties of about 200 liquid-crystalline stationary phases. This is not many if we consider that several thousand liquid crystals are known. Even if we assume that most of them do not meet the requirements for stationary phases, the number that might be utilized is much greater than that tested.

Liquid crystals intended for use as stationary phases must meet different requirements than those designed for other uses, *e.g.*, displays. There exist, however, commercial liquid crystals that can be applied both in mixtures used for displays and in gas chromatography³¹.

Liquid-crystalline stationary phases should have a high thermal stability. They should not decompose at the operating temperature and at that temperature they should have a low vapour pressure. Many liquid crystals meet these requirements, they can retain their properties during many weeks³² and even months³³ or years³⁴ of use in a column. Only a few studies have been concerned with measurements of the vapour pressure of liquid crystals³⁵. From the results it can be seen, however, that the vapour pressure is relatively lower for the mesophase range than for the isotropic liquid. The behaviour of the liquid crystal in the column is largely determined by its adhesion to the support. In this respect liquid-crystalline stationary phases are as good as conventional ones.

The melting points of liquid crystals used as stationary phases should not be lower than about 50°C. The upper limit of the melting point has not been determined. We seek liquid crystals with high melting temperatures that could be used at temperatures above 300°C. Today we already have columns with liquid-crystalline stationary phases that can operate at temperatures below 300°C. In gas chromatography with temperature programming use is made of liquid crystals with a wide mesophase range, low melting point and high clearing temperature³⁶⁻³⁸. In some instances the mesophase range of the liquid crystal is narrow.

The widest mesophase ranges occur in nematic liquid crystals and the latter are the type most often tested as stationary phases. The mesophase range can be extended by using mixtures of liquid crystals. Such mixtures, when used as stationary phases, often show better properties than their individual components^{28,39-48}. Good separation properties are shown by mixed liquid-crystalline stationary phases of eutectic composition. One can also use liquid crystal mixtures obtained directly from synthesis, for instance, the isomers of azoxy compounds^{49,50}. The use of mixed liquid crystals increases the range of their applicability as stationary phases.

Mixed liquid-crystalline stationary phases on supports show a strong tendency to become supercooled, so they can be used at temperatures below their melting points. The mesophase obtained at lowered temperatures due to supercooling shows increased ordering, which leads to better separations. The tendency to become super-

cooled is not specific to mixed liquid-crystalline stationary phases, as in many instances considerable supercooling has been observed for individual liquid crystals.

Apart from mixtures composed solely of liquid crystals, stationary phases consisting of a conventional phase and a liquid crystal have also been tested^{46,51-53}.

In several papers the synthesis of liquid crystals particularly suitable for use as stationary phases was described^{44,54-58}. Commercial liquid crystals are also available as stationary phases for gas chromatography^{59,60}. In Poland liquid-crystalline stationary phases are manufactured on a commercial scale by Chemipan (Warsaw) and marketed by POCH (Gliwice).

A good knowledge of the relationships between the molecular structure and the properties of liquid-crystalline stationary phases should allow the synthesis of liquid crystals with optimal separation properties in the future.

4. COLUMNS WITH LIQUID-CRYSTALLINE STATIONARY PHASES

Liquid-crystalline stationary phases are used in the same columns as conventional stationary phases with respect to both column materials and dimensions. Most tests were performed using common analytical columns several millimetres in diameter. Recently, capillary columns^{52,53,61-79} and micropacked columns⁸⁰⁻⁸³ with liquid-crystalline stationary phases have been increasingly used.

The separation properties of liquid-crystalline stationary phases are so good that for most separations it suffices to use analytical columns. The application of capillaries makes it possible to reduce significantly the length of the columns, to a few metres^{72,78}, and good separations are obtained in a short time. The liquid crystals are deposited on the walls of the capillary columns like other stationary phases. A method has also been applied in which the liquid crystalline stationary phase is obtained directly in the capillary column⁷⁵. The preparation of deactivated capillary columns containing different amounts of cholesteryl cinnamate, allowing the analysis of alcohols, has been described by Heath *et al.*⁷⁶.

The samples fed to the columns containing liquid-crystalline stationary phases are as small as possible in order to avoid disturbing the ordering of the liquid crystal structure. However, this is not a limitation compared with conventional phases, as the amounts normally used for separations on conventional phases using the most commonly applied detectors do not affect the structure of the mesophase or overload the column.

The behaviour of nematic and smectic liquid-crystalline stationary phases with high concentrations of the sample substances dissolved in them and the shapes of the peaks obtained have been studied by Bocquet and Pommier⁸⁴⁻⁸⁷. They found that under these conditions a reversible destruction of the ordering of the stationary phase occurs during the chromatography of large amounts of a substance. Similar investigations were carried out by Maryakhin *et al.*⁸⁸. The effects of various factors and conditions in the column (*e.g.*, size of sample, pressure loss, presence or absence of sorption effects) on the chromatographic separation were studied⁸⁴⁻⁸⁸. It has been found that liquid-crystalline stationary phases can also be used for preparative separations.

The liquid-crystalline stationary phases are usually deposited on supports from solutions by evaporation of the solvent. Good results have also been obtained when

the liquid crystal in the form of a powder was mixed with the support and the mixture was introduced into the column; subsequently the filled column was heated to a temperature higher than the liquid crystal melting point⁸⁹.

The supports used for liquid-crystalline stationary phases are the same as those for conventional stationary phases. It is known that the surface of the support affects the orientation of the liquid-crystalline stationary phase molecules. This effect is greater than with non-liquid-crystalline phases. It has been found, for instance, that the liquid crystal behaves in different ways on glass spheres whose surfaces were subjected to various pre-treatment procedures⁹⁰. The effect of active supports (silica gel, Silochrom) on the properties of liquid-crystalline stationary phases has been studied^{27,91-99}. It seems important from the practical point of view to acquire a knowledge of the properties of liquid crystals deposited on the most frequently used supports, Chromosorbs^{50,95-98}.

The efficiencies of columns containing liquid-crystalline stationary phases are usually lower than those of columns containing non-liquid-crystalline phases, owing to the high mass transfer resistance in the liquid stationary phase. This resistance is caused by the high viscosity of liquid crystals, and it can vary depending on the kind of support used and thus on the different arrangement of the liquid crystal molecules.

5. VARIATION OF RETENTION PROPERTIES WITH COLUMN TEMPERATURE

The first studies of the dependence of retention properties on the temperature of columns containing liquid-crystalline stationary phases showed it is different to that for conventional stationary phases. This has been confirmed for various liquid crystalline stationary phases (nematic, smectic, cholesteric)^{50,67,99-102}. Typical plots of the relationships obtained are shown in Fig. 2.

The retention properties vary from one liquid crystal phase to another. In the temperature range of solid liquid-crystalline stationary phases the retention of a sample substance usually decreases with increasing temperature. When the temperature approximates the transition points to the mesophase and isotropic liquid, a minimum appears on the curve, followed by an increase, often extending over many degrees, to a maximum corresponding to the phase transition. On completion of the transition to the isotropic liquid the curve assumes its normal decreasing character.

It has been assumed that the dependence of retention on temperature shown in Fig. 2 is characteristic of liquid-crystalline stationary phases. This led to the conclusion that it is possible to determine with good accuracy the phase transition temperatures. Later investigations have shown, however, that in some instances the retention relationships do not show phase transitions^{57,58,82,83,91,92,103}. The character of the variation of the retention properties with temperature of columns containing liquid-crystalline stationary phases depends on the kind of support used (physico-chemical surface condition and surface area), the kind of liquid-crystalline stationary phase (chemical and spatial structure of the molecule, structure of the mesophase, heats of phase transition) and the amount of the stationary phase on the support. Although each of these factors is important, the final effect depends on their mutual influence, *i.e.*, on the properties of the liquid crystal-support system as a whole. These properties affect the character and the range of action of the support surface with the liquid-crystalline stationary phase molecules. More active supports (Silochroms, non-sila-

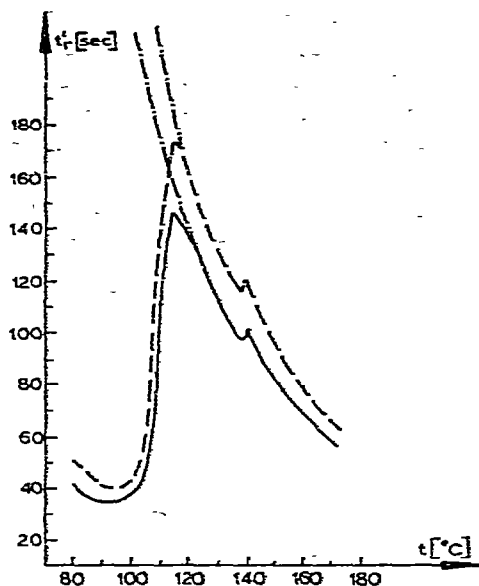


Fig. 2. Dependence of retention times (t_r) of *p*-xylene (solid line) and *o*-xylene (dashed line) on column temperature (t) for 10% 4-hydroxy-4'-ethylazoxybenzene 4-benzoate deposited on Chromosorb W AW during heating; the dash-dot curve corresponds to column cooling.

nized Chromosorbs) react with the liquid crystal molecules more actively than inactive supports (e.g., silanized Chromosorbs). Depending on the structure and physico-chemical character of the liquid-crystalline stationary phase molecule and the kind of support, the stationary phase may form agglomerates. The mean thickness of the layer exposed to the action of the support surface forces may vary over a wide range, e.g., from 2 nm⁹⁷ to 100 nm¹⁰⁴. When agglomerates are formed or when the thickness of the stationary phase layer is so large that the ordering forces in the liquid crystal are not dominated by the support surface forces, the properties characteristic of the liquid crystal and observed in the bulk are manifested at the surface. In this situation retention relationships are obtained that allow the accurate determination of the phase transition temperatures. Not only the phase transition temperature itself can be determined chromatographically but also the temperatures of the transition region. Usually the plots of retention parameters *versus* temperature show the transitions from the solid to the mesophase and from the mesophase to the isotropic liquid. Sometimes the temperatures of transitions from the smectic to the nematic phase and those between the smectic and even nematic types can also be determined^{67,71,105-107}.

Cases are known where the phase transition temperatures determined chromatographically differ from those found by the thermo-optic method. It has been found that the temperatures of phase transition depend largely on the amount of the liquid-crystalline stationary phase on the support⁹⁵. A phase transition was detected below the liquid crystal melting point determined by the thermo-optical method^{95,108}. Similar phase transitions above the melting point were observed by Serpinet for non-liquid-crystalline stationary phases¹⁰⁹.

A knowledge of the phase transition temperatures in liquid crystals on sup-

ports is important from the point of view of their application for analytical purposes. The best separations of mixtures are obtained at temperatures by a few (2-6) degrees higher than the liquid-crystal melting point^{88,110}. It is possible, however, to exploit the column containing the liquid crystal at other temperatures, below the melting point (in the solid range and supercooled mesophase) and in the isotropic liquid above the clearing temperature^{45,61,70-72,81,89,99,111-116}. It was found that the application of active supports may increase significantly the width of the temperature range in which the liquid-crystalline stationary phase yields good separations⁹³.

6. COMMENTS ON THE SEPARATION MECHANISM ON LIQUID-CRYSTALLINE STATIONARY PHASES

The ordering of the liquid-crystalline stationary phase structure is decisive for the separation ability of those phases. From practice we know that compounds in which the molecule length to width ratio is large are retained on the liquid-crystalline stationary phase longer than those with shorter, more compact molecules. Likewise, planar molecules are retained in the column longer than those with a structure differing greatly from planarity^{49,117}. Long and planar molecules fit better the ordered structure of the liquid crystal, whereas non-linear and non-planar molecules do not permeate so easily between the liquid-crystalline molecules of the stationary phase and therefore are more easily eluted from the column. A close interaction occurs between the molecules of the chromatographed substance with those of the liquid-crystalline stationary phase. This is confirmed by the fact that the molecules of the dissolved substance, whose structure is similar to that of the liquid crystal molecules, dissolve in the latter more easily and are retained longer in the column^{32,118,119}.

With conventional, non-polar stationary phases the components of a mixture are eluted in order of their increasing boiling points. Xylene isomers are eluted from such columns in the order *para*, *meta*, *ortho*, their boiling points being 138.5, 139.5 and 144.5°C, respectively. The separation of *para*- and *meta*-isomers, which is particularly difficult to perform, may be easier if a stationary phase of higher polarity is used. With liquid-crystalline stationary phases the order of elution of the components of a mixture with identical or similar boiling points depends on the shape of their molecules; thus the order of elution of xylene isomers is *meta*, *para*, *ortho*. *m*- and *p*-xylene are more difficult to separate than *p*- and *o*-xylene on most liquid-crystalline stationary phases. There exist, however, column fillings containing liquid crystals on which the *para*- and *meta*-isomers are separated better than the *para*- and *ortho*-isomers⁵⁵ (see Fig. 3). This depends largely on the kind and amount of the liquid-crystalline stationary phase deposited on the support. Hence the separation results obtained depend to a greater extent than with conventional stationary phases not only on the properties of the stationary phase but also on those of the whole stationary phase-support system.

The effect of planarity of the molecules of the sample substance on the order of their elution is distinct in the case of cyclohexane, cyclohexene and benzene. These compounds are eluted in the above order from columns containing liquid-crystalline stationary phases. Using conventional stationary phases, the order of elution conforms with the boiling points, *viz.*, benzene, cyclohexane, cyclohexene.

The relationships between the shapes of molecules and the retention param-

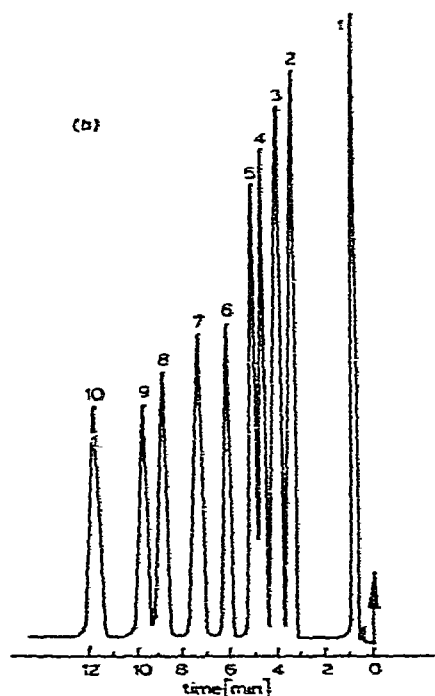
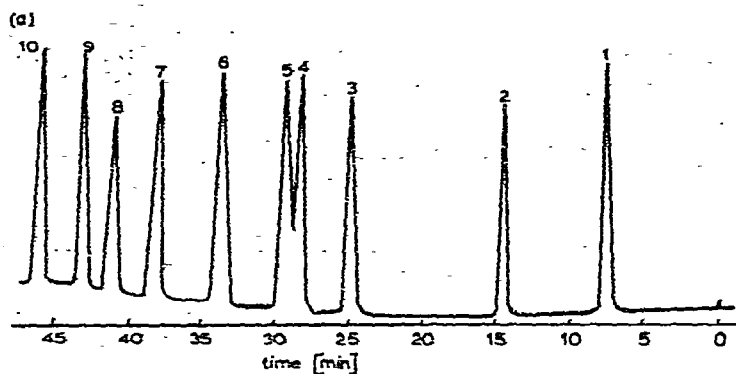


Fig. 3. Two types of xylene separations (in mixtures). (a)¹³⁴ 1 = Benzene; 2 = toluene; 3 = ethylbenzene; 4 = *m*-xylene; 5 = *p*-xylene; 6 = *o*-xylene; 7 = propylbenzene; 8 = *m*-ethyltoluene; 9 = *p*-ethyltoluene; 10 = *o*-ethyltoluene. Azoxybenzene 4-cyano-4'-heptylcarbonate deposited in an amount of 5% on Chromosorb W AW DMCS. Glass column, 5 m \times 4 mm I.D. Initial temperature held at 55°C for 5 min, then increased at the rate of 1°C/min to 120°C. Argon flow-rate, 40 cm³/min. (b)¹⁵¹ 1 = Benzene; 2 = ethylbenzene; 3 = *m*-xylene; 4 = *p*-xylene; 5 = *o*-xylene; 6 = *m*-ethyltoluene; 7 = *p*-ethyltoluene; 8 = *m*-diethylbenzene; 9 = *o*-diethylbenzene; 10 = *p*-diethylbenzene. Bis(4-methylene-4'-*n*-butoxy-2'-methylazobenzene) deposited in an amount 15% on Chromosorb W NAW. Glass column, 3.1 m \times 3 mm I.D. Column temperature, 120°C; argon flow-rate, 20 cm³/min.

ters of compounds chromatographed on liquid-crystalline stationary phases are so close that Radecki *et al.*¹²⁰ found relationships allowing the prediction of the retention indices of polycyclic aromatic hydrocarbons (PAHs) on nematic phases. They also derived an equation for the determination of the molecular shape parameter from chromatographic data. The effects of various factors, including the shapes of molecules, on the retention of PAHs on conventional and nematic liquid-crystalline stationary phases were studied by Bartle *et al.*¹²¹

The interactions of substances dissolved (chromatographed) in the liquid-crystalline solvent (stationary phase) have been studied in detail^{103,118,122-126}

Certain differences are observed in the properties of liquid-crystalline stationary phases depending on the structure of the mesophase. However, most work has been devoted to nematic liquid-crystalline stationary phases, and it is only in recent years that greater attention has been paid to smectic phases.

The results of physico-chemical studies and the thermodynamic data obtained allowed the interpretation of the dissolution mechanism of different classes of compounds in nematic liquid crystals, account being taken of energy changes in the vibrational, rotational and translational movements in connection with the magnitude of the activity coefficient¹²². The solubility in a liquid crystal is the greater the greater is the change of translational energy on passing to the solution and the smaller is the activity coefficient. The solubility is the poorer the greater is the loss of energy of the rotational and vibrational movements which contribute to the growth of the activity coefficient. The partial molar dissolution enthalpy can be expressed by the equation

$$\Delta \bar{H}_2 = \Delta E_{\text{trans}} + \Delta E_{r,v} - RT$$

where ΔE_{trans} is the loss of translational energy of the dissolved substance on reaction with the solvent and $\Delta E_{r,v}$ is the loss of rotational and vibrational movement energy. The sum of those two quantities is the loss of internal energy of the dissolved substance on passing from the gaseous to the liquid state. Both of these quantities are negative, which is in accordance with the exothermic character of the dissolution process.

Dissolution in the mesophase requires greater energy than dissolution in the isotropic liquid of the same substance, as the domination of spatial limitations on the permeation of molecules of the dissolving substance into the ordered structure requires adequate energy. Kelker and Verhelst¹²⁷ advanced a rule stating that the excess of free enthalpy of the dissolved substance and the heat of dissolution in the mesophase are more positive than the corresponding values for the isotropic phase. The heats of mixing in mesophases are several kilojoules per mole higher than those in isotropic liquids^{36,41}.

Liquid-crystalline stationary phases show a particular affinity to linear molecules of the dissolving substance. *n*-Alkanes with long chains, however, show a higher free enthalpy than, for instance, xylenes. The molecules of the former are elastic and the chains must straighten and become rigid to allow maximum interaction with the liquid-crystal structure; in contrast, xylene molecules are already sufficiently rigid^{119,128}.

The separation capacity of liquid-crystalline stationary phases, related to the

differing solubilities of molecules with different shapes, has been repeatedly studied for *meta*- and *para*-disubstituted benzene isomers, especially xylenes. The mechanism of the chromatographic separation of disubstituted benzene isomers and of other compounds on nematic liquid-crystalline stationary phases was discussed in detail by Martire *et al.*¹²⁹, Kraus *et al.*⁶³, Oweimreen *et al.*^{124,130} and Rippie and Ibrahim¹³¹. In the nematic phase the *para*-isomer of the disubstituted benzene derivative reveals in most instances the greatest partial molar dissolution enthalpy and the smallest activity coefficient among the three isomers. In view of their shape, polarity and polarizability, the *para*-isomers lose most translational energy. Enthalpy and not entropy is the factor that lowers the activity coefficient and increases the retention time of the *para*-isomers, although the *para* isomers fit better the ordered structure of the nematic phase.

Janini and Ubeid¹³² studied the thermodynamics of dissolution of phenanthrene and anthracene in a nematic liquid crystal and in an isotropic stationary phase. Their conclusions conform with those drawn by other workers for compounds with lower molecular weights.

The thermodynamics of the solutions and the separation effects obtained on cholesteric stationary phases are related to the similarity of their structure and also to its difference from that of nematics^{101,119,123}. Epimers of steroids can be separated on nematic stationary phases¹³³; however, more selective towards steroids are cholesteric cholesterol esters whose molecules are not as elongated or as polar as the molecules of nematics³².

The suitability of cholesteric stationary phases for the separation of isomers was tested in normal analytical columns^{14,41,134} and in capillary columns^{65,73,76}. Alkylbenzene isomers separate worse on cholesteric phases than on nematic and some smectic phases^{14,41,73,134}. Cholesteric liquid crystals show higher selectivity towards *cis*- and *trans*-isomers of *n*-alkenes than nematic, smectic and also non-liquid-crystalline stationary phases⁷³. With nematic stationary phase good separations of *cis*- and *trans*-isomers was obtained when the nematic had a *trans*-configuration³¹. Such a phase also gave good separations of alkylbenzene isomers.

The dissolution mechanism of *para*-isomers using smectic liquid-crystalline stationary phases is different to that on nematic phases¹⁰⁷. On passing from the gaseous to the mesomorphous phase the molecule loses its vibrational-rotational energy, the losses being the greater the higher is the degree of ordering of the mesophase. Both the higher dissolution enthalpy and the higher activity coefficient of the more ordered phase indicate this effect. When the ordering of the smectic phase decreases, its dissolving ability increases. This has been confirmed for a number of smectics A, B and C⁶⁷ and A, C, F and G¹⁰⁷. In highly ordered phases the *para*-isomers have a lower dissolution enthalpy and activity coefficient than the *ortho*- and *meta*-isomers. It follows that the loss of the vibrational-rotational energy of the *para*-isomer is lower than those of the remaining isomers.

In most instances the process of dissolution in mesophases was studied at infinite dilution of the chromatographed substance in the stationary phase, typical for chromatography. However, certain thermodynamic quantities relating to the dissolution of finite amounts of various compounds in the smectic, nematic and isotropic liquid have also been determined^{86,87,130}. Earlier conclusions have also been confirmed regarding the dissolution mechanism and energy of chromatographed substances in the particular kinds of mesophase.

The effect of the degree of ordering of the liquid crystal on the separations obtained is large. Therefore, the best separations are usually obtained at the lowest temperature of the mesophase (with the exception of smectics of the highest degree of ordering) or in the supercooled mesophase, when its ordering is highest. Higher selectivity is also obtained on those liquid crystals whose mesophase range is wide and the transition temperature from the mesophase to the isotropic liquid is high^{15,135,136}. A correlation exists between the relative retentions of *para*- and *meta*-xylenes depending on the mesophase range¹⁷. The wide range of the mesophase points to the occurrence in it of highly ordering intermolecular forces which are not easy to dominate by thermal action. Thus the separations carried out on these phases are usually good.

It is commonly assumed that nematic stationary phases have better separating properties than smectic phases. It has been observed, however, that sometimes good separations are also obtained on smectic phases^{42,55,137,138}. More accurate studies carried out recently have allowed an explanation of this problem. The kind of smectic phase is decisive for its separation efficiency. Good separations are obtained on less ordered smectics (e.g., A and C), whereas much poorer separations were obtained on more ordered phases (e.g., B)^{139,140}. Phenanthrene and anthracene are better separated on smectic phases A and C than on nematic phases^{138,139}. Likewise, alkylbenzene and *n*-alkene (C₁₀-C₁₃) isomers separate better on these smectic phases than on nematics⁷¹.

It would have been expected that as in nematics an increase in ordering of the smectic mesophase will cause an increase in its separating capacity. The examples given show, however, that this is not always so and that smectics of the highest degree of ordering always have a low separating capacity. One of the reasons is the laminar structure of the smectic mesophases with a compact arrangement of molecules in the layers. The dissolved molecules cannot penetrate into the layer and dissolve by entering between the layers¹⁴. The interlayer region is a zone of relatively weak intermolecular attractive forces and therefore it is more easily accessible but less selective. The liquid-crystalline smectic phase therefore often has a lower dissolving capacity and lower selectivity than the nematic phase. Sometimes a compound with two smectic phases behaves so that the phase occurring at the higher temperature and revealing a poorer ordering of the molecules in the layer is more selective. The high selectivity of smectic compounds may be due to interlayer dissolution, the adsorption of some molecules (e.g., *para*-isomers) being given preference by the terminal groups present at the surface of the liquid-crystal layers.

The significant effect of the support surface on the properties of liquid-crystalline stationary phases allows us to assume another explanation for the lower selectivity of highly ordered smectic liquid crystals compared with the nematic ones. In nematics there is no ordering in the layers, so the molecules in the domains can become arranged on a surface chemically and geometrically non-homogeneous without the deformations required in the case of smectics, especially those which are highly ordered. In the latter the layers must be "broken" to fit the structure of the support surface, so as a result the ordering of the molecules on the support is lower than beyond it and possibly even lower than in the case of the nematic mesophase. If we assume this mechanism, the observed high selectivity of less ordered smectic liquid crystals may be explained by the smaller disturbance of their structure by the surface of a low-activity support.

Some information about the separation mechanism of nematic and cholesteric stationary phases is obtained from investigations carried out using an electric field applied perpendicular to the walls of capillary columns^{68,69,141-147}. A constant electric field improved the ordering of the mesophase, orienting the molecules horizontally or vertically to the column wall, depending on the dielectric anisotropy sign. The ordering of the mesophase increased by the electric field allows us to obtain better separations of mixtures owing to the improved symmetry of the peaks and increased partition coefficients. At the same time the retention time and HETP decrease⁶⁸. The effects obtained are, however, fairly small. More important is the finding that the electric field induces the adsorption of polar compounds such as esters, ketones, aldehydes and halogenobenzenes^{68,69,145,146}. The adsorption increases linearly with increasing intensity of the field applied. It depends on the kind of compound and is closely related to its dielectric constant. On this basis a relationship was derived for calculating these constants. The calculated values are similar to those given in the literature^{69,145}. With isomers of benzene derivatives, the *ortho*-isomer is more strongly adsorbed than the others.

Detailed investigations have shown that the adsorption of a polar compound (alcohols or ethers) depends largely on the structure of the carbon skeleton and the position of the hydroxy group in the molecule⁷⁷. It has been found that adsorption decreases with increasing number of side-chains in the carbon skeleton. Adsorption also decreases when the hydroxy group is located in the vicinity of the side-chains or in the middle of the carbon chain. With butanol isomers adsorption decreases in the order *n*- > *iso*- > *sec*- > *tert*-. This shows that the structural factor must be accounted for when calculating the dielectric constants from adsorption data for liquid crystals in an electric field.

It is assumed that adsorption in an electric field takes place on the nematic existing initially or on the nematic generated under the action of the field. This is probably the reason why the same adsorption is obtained at a voltage of several dozen volts on nematics and at a voltage of several hundred volts on cholesterics (which are transformed into nematics).

The adsorption is not influenced by the size of the sample, and is constant for a given column filling and applied voltage. Solvents do not affect adsorption directly, but a polar solvent may displace the compounds adsorbed earlier.

The possibility of separating polar and non-polar compounds may be the basis for a new technique of separation and identification of chemical compounds by gas chromatography. Good analytical effects were obtained when a column containing a conventional stationary phase was combined with a short column filled with liquid crystals to which an electric field was applied. Such a system of columns was applied for determining hydrocarbons.

In addition to the major role of the liquid crystal structure and the shape of the molecules to be separated, the separations obtained are influenced by many other factors, which are often decisive in chromatographic processes involving conventional stationary phases. The properties of the separated substances that deserve particular attention are their boiling points and the size, polarity, polarizability and elasticity of the molecules. As regards a liquid-crystalline stationary phase, the chemical structure and the related polarity affect the results obtained. The polarity of most liquid-crystalline stationary phases is low or medium. When it is determined from the

retention index according to Rohrschneider¹⁴⁸ and McReynolds¹⁴⁹, the difference in retention indices for *para*- and *meta*-xylene is additionally introduced^{114,150,151}. This difference characterizes the liquid crystal better than polarity itself.

The process of separation on liquid-crystalline stationary phases is the overall result of the properties of the chromatographed substance and stationary phase and their mutual interactions. In some instances this may be a charge transfer³⁷.

7. EXAMPLES OF SEPARATIONS ON LIQUID-CRYSTALLINE STATIONARY PHASES

Various mixtures, including mixtures of numerous isomers, have been separated on liquid crystalline stationary phases and the results obtained were far superior to those obtained on the conventional stationary phases used hitherto. A direct comparison of the possibilities of separating isomers on liquid-crystalline and conventional stationary phases^{75,152} including Bentone³⁴ (regarded until recently as the best stationary phase for separations of isomers^{153,154}) was in favour of the liquid-crystalline phase. Among the separated mixtures were isomers of various disubstituted benzene derivatives (e.g., xylene and toluene derivatives)^{13,14,31,61,63,70-72,78,82,83,89,94,99,100,150,155-160}, phenol derivatives^{161,162}, dimethyl esters of phthalic acid⁷⁸ and vinylbenzenes¹⁶³. Terpenes and odorants¹⁶⁴, steroids^{32,66,133,165,166}, bile acids¹⁶⁶, hydroxy, alkyl, halogen and amino naphthalene derivatives^{51,64,89,94,99,103,113,114,118,160,167-169}, chlorinated biphenyls^{66,170,171}, pesticides⁶⁶, methoxyquinone derivatives¹⁷², and methylpyridine derivatives¹⁶⁰ have been analysed on liquid-crystalline stationary phases. In several works it has been shown that these stationary phases are also suitable for separating geometric isomers, e.g., the isomers of *Z*- and *E*-pheromones and of unsaturated fatty alcohols and their derivatives^{65,76,137,172}, and methyl esters of unsaturated fatty acids³¹. The *cis*- and *trans*-isomers of *n*-alkenes^{73,74} and disubstituted cyclohexane derivatives³¹ were separated, the *cis*-isomer usually being eluted before the corresponding *trans*-isomer.

In recent years, particular attention has been paid to liquid-crystalline stationary phases with broad mesophase ranges and high melting points. These are used for the separation of polynuclear aromatic hydrocarbons (with up to seven rings), including carcinogenic compounds^{25,28,37,52,55,56,66,75,80,89,103,111,135,138,139,160,167,173-180}. Hall and Mallen separated on high-melting liquid-crystalline stationary phases benefin and trifluralin¹⁸¹ and the isomers of benoxaprofen¹⁸², and Pailer and Hložek separated azoheterocyclic compounds³⁸. Liquid-crystalline phases have also been applied to the determination of the purity of liquid crystals¹⁸³.

Many of the separations carried out on liquid-crystalline stationary phases are important for industry (petroleum and coal chemistry) and in the analysis of environmental pollutants^{78,138,168}, including isomers of phenyl derivatives. These isomers were converted into ether or acetyl derivatives to increase the possibility of separation of composite mixtures^{161,162}.

The initial predictions that liquid crystals will allow the separation of optical isomers remained unrealized for a long time. It was only in 1973 that Lochmüller and Souter succeeded in carrying out such separations¹⁸⁴. The enantiomers of *N*-perfluoroacyl derivatives of 2-aminoethylbenzene, 2-amino-3-phenylpropane and 2-amino-4-phenylbutane were separated on optically active esters of carbonyl-bis-valine and carbonyl-bis-leucine¹⁸⁴⁻¹⁹⁰. Separations of these compounds, although of

lower quality, were also carried out on the isotropic phase of the mentioned liquid crystals.

It has already been mentioned that liquid-crystalline stationary phases can be used in the supercooled state. In this state retention times reproducible for many hours are obtained for components of the separated mixtures. It has been found that the following procedure allows retention times reproducible for many days and separations of mixtures to be obtained. After heating the column in the chromatograph to about 5°K above the boiling point it is cooled, for instance, by 5°K per 10 min, until the required supercooling temperature is reached. After switching off the apparatus and cooling the column, one proceeds after about 12 h (e.g., the next day) as described earlier. The separations of mixtures in the supercooled state obtained are superior to those obtained in the range of the mesophase; however, the separation times are considerably longer. For analytical purposes the supercooled nematic state is chiefly used^{49,81,113}, because the nematic mesophase supercools more easily than the smectic phase and the supercooling is usually deeper. Use is also made of the supercooled cholesteric phase, in which in a capillary column increases in the separation factor, the partition coefficient, the column efficiency per unit length and the resolution are observed⁷⁶.

In Fig. 4 the separations of mixtures on liquid-crystalline and isotropic liquid phases are compared. It can be concluded that the liquid-crystalline stationary phases are largely universal. They can be used for the separation of mixtures of many groups of chemical compounds, and allow the separation of mixtures of isomers and compounds that are not isomers.

Further extension of the applications of liquid crystals in chromatography is possible by their use as stationary phases in liquid chromatography¹⁹¹. It seems, however, that polymeric liquid crystals may be more suitable for liquid chromatography, and their use in gas chromatography cannot be excluded.

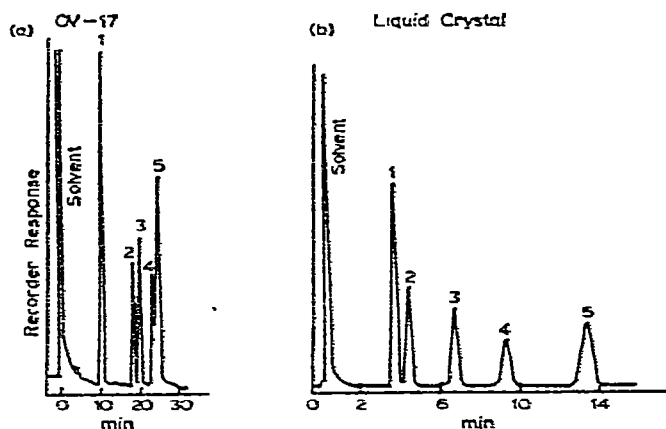


Fig. 4. Separation of 1-, 2-, 3- and 4-methoxybenzanthraquinones¹⁷¹. (a) Column, 6 ft. \times 2 mm I.D.; packing, 5% OV-17; oven temperature, 262°C; flow-rate, 60 cm³/min. (b) Column, 6 ft. \times 2 mm I.D.; packing, 2.5% BPhBT; oven temperature, 262°C; flow-rate, 60 cm³/min. Peaks: 1 = 7,12-Benzanthraquinone; 2 = 1-CH₃O-BATQ; 3 = 2-CH₃O-BATQ; 4 = 4-CH₃O-BATQ; 5 = 3-CH₃O-BATQ.

A detailed list of liquid-crystalline stationary phases and the separations obtained is given in Table I.

8. INVESTIGATION OF THE PROPERTIES OF LIQUID CRYSTALS BY GAS CHROMATOGRAPHY

Chromatographic physico-chemical investigations facilitate the explanation of the phenomena taking place in the course of a chromatographic process and contribute to a better knowledge of the properties of liquid-crystalline stationary phases and liquid crystal-support systems. Gas chromatography has many advantages as a method for physico-chemical investigations, including simplicity of the apparatus involved, good control of temperature, the possibility of operating in a wide temperature range, rapid determinations and the possibility of measuring various quantities at low concentrations of the chromatographed substances^{122,198,199}. These advantages are accompanied by a high sensitivity of the sorption characteristics and the related retention parameters of the analysed substances, varying with the state of the liquid crystal phase. From the measured retention relationships, many quantities can be determined that characterize the liquid-crystalline stationary phase itself and the chromatographed substance-liquid crystal system. Particularly interesting are the phenomena occurring in the transition zones. They are related to the increase in the solubility of the chromatographed substance due to the decrease in the free energy of the solution on transition to a less ordered structure. In the region of the phase transition many features of the liquid crystal undergo changes, viz., the vapour pressure, specific heat, density, coefficient of thermal expansion, surface tension, viscosity and diffusional and thermodynamic properties. At least some of these can be measured chromatographically.

The activity coefficients of a substance dissolved in a liquid crystal obtained from chromatographic measurements show good agreement with the values obtained by static methods²⁰⁰. The values of these coefficients are different in the particular phases of the liquid crystal^{82,125,201}. It has been found that the variation of the activity coefficient (f) of a chromatographed substance and of the clearing temperature of various liquid crystals expressed as $\ln f = f(1/T)$ is linear²⁰².

The enthalpies and entropies of various substances in liquid-crystalline stationary phases have been measured^{33,63,84,103,122,139,163,201}. A linear dependence of the partial molar enthalpy of the solution on the partial molar entropy of that solution was found for the alkane homologous series, *n*-1-alkenes and *n*-1-chloroalkenes in 4,4'-azoxyanisole¹²² and for various compounds in cholesteryl palmitate²⁰¹. The chromatographically measured thermodynamic quantities provide information on the interaction of molecules with nematic liquid-crystalline stationary phases²⁰³.

Chromatographic studies have also provided information about the effect of various substances dissolved in cholesteric liquid crystals on the structure of the mesophase and the related changes in the reflected light wavelength²⁰⁴.

Certain theoretical aspects of the displacement of the chromatographic band of a substance dissolved in a column containing a liquid-crystalline stationary phase have been elucidated and related to various types of partition isotherms and the effect of sorption and also to the process of distribution in the mesophase⁸⁴⁻⁸⁷. The par-

TABLE I

EXAMPLES OF LIQUID-CRYSTALLINE STATIONARY PHASES AND MIXTURES SEPARATED ON THEM

Stationary phase	Transition temperature to phase (°C)				Separated substances	Refs.
	Smectic	Nematic	Cholesteric	Isotropic		
4,4'-Azoxyphenetol		138		168	Benzene, toluene, ethylbenzene, xylene isomers	11
4,4'-Azoxyanisole		120		135	Disubstituted benzene	13
4,4'-Dihexyloxyazoxybenzene	71	80		130	isomers	
4,4'-Diheptyloxyazoxybenzene	75	95		127		
<i>trans-p</i> -[5-(4- <i>n</i> -Heptylcyclohexyl)-2-pyrimidinyl]benzonitrile		80		226	<i>cis</i> - and <i>trans</i> -1-(4'-propylphenyl)-4-propylcyclohexane. Methyl esters of palmitoleic acid and of palmitelaic acid. Methyl esters of oleic acid and of elaidic acid. Ethylbenzene, xylene isomers	31
Cholesteryl benzoate			150	178	Steroid isomers (andro-	32
5- α -Cholestan-3 β -yl benzoate			137	155	stanes, androstenes,	
Cholesteryl <i>p</i> -phenylbenzoate			178	290	cholestanes and cholestenes	
N,N'-bis(<i>p</i> -methoxybenzylidene)- <i>x,x'</i> -bi- <i>p</i> -toluidyne (BMBT)		181		320	Polynuclear aromatic hydrocarbons	37
BMBT		181		320	Aza-heterocyclic compounds	38
4-Cyano-4'-pentyloxyazoxybenzene		93.5		146.5	Cyclohexane, cyclohexene,	49
4-Cyano-4'-octyloxyazoxybenzene	71	117		135	benzene, disubstituted benzene isomers	
Azoxybenzene 4-cyano-4'-pentylcarbonate		52.5		132.5	(alkylbenzenes, halogenobenzenes and alkylhalogenobenzenes)	
Azoxybenzene 4-cyano-4'-octylcarbonate	61.5	112		127.5		
4-Cyano-4'-pentyloxyazobenzene		106		116.5		
4-Cyano-4'-octyloxyazobenzene		101		111		
N,N'-Bis(<i>p</i> -butoxybenzylidene)- <i>x,x'</i> -bi- <i>p</i> -toluidine (BBBT) (pure and in mixture with SE-52)	159	188		303	Polynuclear aromatic hydrocarbons	52
N,N'-Bis(<i>p</i> -phenylbenzylidene)- <i>x,x'</i> -bi- <i>p</i> -toluidine (BPbBT)		257		403	Polynuclear aromatic hydrocarbons	55
N,N'-bis(<i>p</i> -hexylbenzylidene)- <i>x,x'</i> -bi- <i>p</i> -toluidine (BHxBT)	127	229		274		
BPbBT		257		403	Polynuclear aromatic hydrocarbons	56
BBBT	159	188		303		
4-Hydroxy-4'-ethylazobenzene		138		292	Saturated and unsaturated aliphatic hydrocarbons	57
4-cyanobenzoate						
4-Hydroxy-4'-ethylazoxybenzene		114		> 306	Cyclohexane, cyclohexene, benzene, toluene, ethylbenzene, propylbenzene	
4-cyanobenzoate						
4-Hydroxy-4'-ethylazobenzene		108		250	Isomers of disubstituted benzene derivatives	
4-methylbenzoate						
4-Hydroxy-4'-ethylazoxybenzene		87.5		250.5	Esters	
4-methylbenzoate					Ketones	
					Naphthylamines	

(Continued on p. 328)

TABLE I (continued)

Stationary phase	Transition temperature to phase (°C)				Separated substances	Refs.
	Smectic	Nematic	Cholesteric	Isotropic		
4,4'-Azoxyphenetole		138		168	Mono- and dimethylnaphthalene isomers	64
Cholesteryl cinnamate			160	210	Geometrical isomers of olefinic aliphatic insect pheromones	65, 76
BPhBT		247		403	Polynuclear aromatic hydrocarbons	66
BBBT	159	188		303		
4- <i>n</i> -Pentylacetophenone (O-4- <i>n</i> -octyloxybenzoyloxime)		48		96	Xylene, <i>n</i> -decene, <i>n</i> -undecene, <i>n</i> -dodecene, <i>n</i> -tridecene isomers	70
5- <i>n</i> -Heptyl-2-(4- <i>n</i> -nonyloxyphenyl)pyrimidine	45.5	56.5		70	Xylene, <i>n</i> -decene, <i>n</i> -undecene, <i>n</i> -dodecene, <i>n</i> -tridecene isomers	71
<i>p</i> - <i>n</i> -Heptyloxyphenyl-4-(<i>trans</i> -4- <i>n</i> -propylcyclohexanecarboxyloxy)2-methylbenzoate		65		145	Benzene, toluene, ethylbenzene, xylene isomers	72
Cholesteryl butyrate			102	113	<i>n</i> -Decene, <i>n</i> -undecene, <i>n</i> -dodecene, <i>n</i> -tridecene isomers	73
<i>p</i> - <i>n</i> -Heptyloxyphenyl-4-(<i>trans</i> -4- <i>n</i> -propylcyclohexanecarboxyloxy)2-methylbenzoate		65		143	Dimethyl esters of benzene dicarboxylic acid isomers	78
4- <i>n</i> -pentylacetophenone(O-4- <i>n</i> -pentyloxybenzoyloxime)		63		94	Isomers of <i>n</i> -tridecenes and <i>n</i> -tetradecenes	79
BPhBT		247		403	Polynuclear aromatic hydrocarbons	80
4-Cyano-4'-pentyloxyazoxybenzene (one isomer)		124		153	Dichlorobenzene, bromotoluene, chlorotoluene isomers	81
4-Cyano-4'-pentyloxyazoxybenzene (isomer mixture)		94		141.5	Xylene isomers	
4-Cyano-4'-octyloxyazoxybenzene (one isomer)	101.5	137		151.5	Diethylbenzene isomers	
Azoxybenzene 4-cyano-4'-hexylcarbonate		73		137	Saturated and unsaturated aliphatic hydrocarbons, cyclic hydrocarbons	83
Azoxybenzene 4-cyano-4'-nonylcarbonate	61	124		127	Esters	
Azoxybenzene 4-cyano-4'-derylcarbonate	74			125.5	Ethers	
					Hydrocarbon chloro derivatives	
					Disubstituted benzene isomers	
Cholesteryl pelargonate			78	91.5	<i>cis</i> - and <i>trans</i> -Decalin	92
<i>n</i> -Amyl-4- <i>p</i> - <i>n</i> -nonyloxybenzylideneamine cinnamate		80		135	Xylene isomers	
4-Methoxy-4'-ethoxyazoxybenzene		91.5		150	Cyclohexane, benzene, <i>n</i> -heptane, isooctane, toluene, <i>n</i> -octane, <i>m</i> -xylene	99
4-Methoxybenzylidene-4'-butyrylaniline		53		111	<i>p</i> -Xylene, <i>n</i> -nonane, vinyltoluene isomers	
Bisphenetidyterephthalic aldehyde						

TABLE I (continued)

Stationary phase	Transition temperature to phase (°C)				Separated substances	Refs.
	Smectic	Nematic	Cholesteric	Isotropic		
					Benzene, toluene, ethylbenzene, <i>m</i> -xylene, <i>p</i> -xylene, isopropylbenzene, <i>o</i> -xylene	
					Dimethylnaphthalene isomers (2,6 and 2,7, 2,3-, 1,5- and 1,4-, 1,3- and 1,6-)	
4-Methoxy-4'-ethoxyazoxybenzene		91.5		150	Benzene, toluene, ethylbenzene, xylene isomers	100
1-(4-Methoxybenzenoazo)-4-hydroxynaphthalene toliate				212	Mono- and dimethylnaphthalene isomers	103
Bis(4-methylene-4'-hydroxyazobenzene) valerate	165	184		303	1,2,4,5-Tetraethylbenzene, naphthalene, diphenyl ether, acenaphthene, benzophenone, phenanthrene, anthracene, Phenanthrene, anthracene, carbazole	
					Naphthols	
					Decylbenzene, decylaniline, decylacetophenone	
Ethylene 4,4'-diphenylbis(4-methoxybenzoate)		163		302	<i>p</i> -Xylene, <i>o</i> -xylene, naphthalene, benzo [δ]thiophene, 2,7-, 2,6-, 1,5-dimethylnaphthalenes, phenanthrene, anthracene	111
BMBT		181		320	Mono- and dialkylnaphthalene isomers	113
Azoxybenzene 4-cyano-4'-octylcarbonate	60.5	119.5		125.5	Cyclohexane, cyclohexene, benzene, toluene, ethylbenzene, xylene isomers, propylbenzene, ethyltoluene isomers	117
BMBT		181		320	Steroid epimers	133
Azoxybenzene 4-cyano-4'-heptylcarbonate		66		130.5	Pentane, hexane, heptane, octane, nonane, decane	134
					Benzene, toluene, ethylbenzene, xylene isomers, propylbenzene, ethyltoluene isomers, chlorotoluene isomers, dichlorobenzene isomers, bromotoluene isomers	
BBBT	159	188		303	Polynuclear aromatic hydrocarbons	135
Diethyl 4,4'-azoxydicinnamate	136			260	Dodecadienyl and tetradecadienyl acetates	137
Bis(4-methylene-4'- <i>n</i> -butylbenzoyloxyazobenzene)	195	217		350	Polynuclear aromatic hydrocarbons (fluorene, phenanthrene, anthracene, carbazole; quantitatively)	138

(Continued on p. 330)

TABLE I (continued)

Stationary phase	Transition temperature to phase (°C)				Separated substances	Refs.
	Smectic	Nematic	Cholesteric	Isotropic		
N,N'-Terephthalylidene-bis-(4- <i>n</i> -butylaniline)	112	198		235	Fluorene, phenanthrene, anthracene, 1-methylbenanthrene, 9-methylanthracene, methylanthracene	139
N,N'-Terephthalylidene-bis-(4-ethylylaniline)	126	149		248		
4-Methoxy-4'-ethoxyazoxybenzene		91.5		150	Paraffin and naphthene hydrocarbons, benzene, toluene, ethylbenzene, xylene isomers	150
4,4'-Azoxydianisole		120		135		
4,4'-Azoxydiacetole		138		168	Disubstituted benzene isomers	155
4,4'-Biphenylene bis-[<i>p</i> -(heptyloxy)benzoate]	150	211		315		
2-(4-Ethoxyphenyl)-5-(4-ethylphenyl)pyrimidine		153		214	Disubstituted benzene isomers, β - and γ -picoline	156
2,5-Bis-(4- <i>n</i> -hexyloxyphenyl)pyrimidine	120			216		
2,5-Bis-(4- <i>n</i> -hexylphenyl)pyrimidine	104			185		
2-Phenyl-5-(4- <i>n</i> -octyloxyphenyl)pyrimidine	84			162		
4-Methoxy-4'-ethoxyazoxybenzene		91.5		150	Benzene, toluene, ethylbenzene, xylene isomers	157
Bisphenetidylterephthalic aldehyde					Vinyltoluene isomers Dimethylnaphthalene isomers (2,6- and 2,7-, 1,6- and 1,3-, 2,3-, 1,5- and 1,4-)	
2-Methyl-4'-butyl-4-(4- <i>n</i> -butoxybenzoyloxy)azobenzene		90		175	Ethylbenzene, xylene isomers	159
2-Methyl-4'-methoxy-4-(4- <i>n</i> -butoxybenzoyloxy)azobenzene		108		223	Anisole, methylanisole isomers	
4-[(4-Methoxybenzylidene)-amino]phenyl acetate		80		108	Methylphenols, methoxyphenols, 161 chlorophenols and their alkyl ether isomers	
4-(4-Ethoxyphenylazo)phenyl undecylate		65		110		
4-(4-Ethoxyphenylazo)phenyl heptanoate		60		119		
4-[(4-Methoxybenzylidene)-amino]phenyl benzoate		118		168		
4-Methoxybenzyl-4'-aminoazobenzene		151		185	Mono- and dimethylphenol derivatives	162
<i>p</i> -Phenylene bis-4- <i>n</i> -heptyloxybenzoate	83	125		204	Hydrocarbon isomers (e.g., cymene) and their derivatives (e.g., cresol, methylacetophenone, chlorophenol) and terpenes	164
<i>p</i> -(<i>p</i> -Ethoxyphenylazo)phenyl crotonate		110		197		
Cholesteryl cinnamate			162	216		
BPhBT		247		403	Steroids	165
BPhBT		247		403	Mixture of 5 α / β -cholestan-3 α / β -ols Androstadien-3,17-dione isomers	166

TABLE I (Continued)

Stationary phase	Transition temperature to phase ($^{\circ}\text{C}$)				Separated substances	Refs.
	Smectic	Nematic	Cholesteric	Isotropic		
					Monofunctional methyl esters of cholanic acid, monofunctional cholestanes, cholesterol	
					Mono-, di- and trihydroxy and/or keto methyl esters of cholanic acid and cholesterol	
Bis(4-methylene-4'-hydroxyazobenzene) valerate	165	184		303	Chloronitrobenzene isomers	167
1-(4-Methoxybenzenoazoxy)-4-hydroxynaphthalene toillate		182.5		228	Polynuclear aromatic hydrocarbons	
					Naphthylamines	
					Mono- and dimethylnaphthalenes	
4-Cyanobenzoate-4-hydroxy-4'-ethylazoxybenzene		115		294	Naphthylamines, quantitatively	168
2-Methyl-4'-methoxy-4-(ethoxybenzoyloxy)azobenzene		125		244	Biphenyl, monochlorobiphenyls	169
					Naphthols	
					Naphthylamines	
BPhBT		247		403	7,12-Benzanthraquinone,	171
BBBT	159	188		303	1-,2-,3- and 4-methoxybenzanthraquinones	
					Monomethoxydibenz[<i>a,h</i>] and -[<i>a,j</i>]anthraquinones	
					Mono- and dimethoxyanthraquinones	
4-(<i>p</i> -Methoxycinnamyloxy)-4'-methoxyazobenzene		167.5		> 340	<i>Z</i> - and <i>E</i> -isomers of pheromones and related unsaturated aliphatic alcohols and their derivatives	172
BPhBT		247		403	Benzo[<i>a</i>]pyrene and other hydrocarbons in cigarette smoke	174
BBBT	159	188		303	Polynuclear aromatic hydrocarbons (3-5 rings)	175
N,N'-Bis(<i>p</i> -methoxyphenylbenzylidene)- α,α' -bi- <i>p</i> -toluidyne		247		370	Fluorene, phenanthrene, anthracene, 1-methylphenanthrene, 9-methylanthracene	176
					Methylchrysenes, chrysene	
BPhBT		257		403	Benzo[<i>a</i>]pyrene in petroleum products (quantitatively)	192
4-Methoxy-4'-ethoxyazoxybenzene		91		150	Xylene isomers	193
<i>n</i> -Alkoxyphenylcarbonyloxyphenyl <i>n</i> -alkoxybenzoates					Isomers of methyl esters of toluic acid	194
<i>n</i> -Alkoxyphenylcarbonyloxy-(2-alkyl)phenyl <i>n</i> -alkoxybenzoates						

(Continued on p. 332)

TABLE I (continued)

Stationary phase	Transition temperature to phase (°C)				Separated substances	Refs.
	Smectic	Nematic	Cholesteric	Isotropic		
<i>n</i> -Hexyloxyphenylcarbonyloxyphenyl- <i>n</i> -hexyloxybenzoate					Cresol isomers	195
<i>n</i> -Heptyloxyphenylcarbonyloxyphenyl- <i>n</i> -heptyloxybenzoate						
<i>n</i> -Octyloxyphenylcarbonyloxyphenyl- <i>n</i> -octyloxybenzoate						
N-[4-(<i>p</i> -Methylbenzyloxy)benzylidene]- <i>p</i> -butylaniline		131.5		147	Isomers of disubstituted benzene derivatives	196
Cholesteryl butyrate					Isomers of alkylbenzenes	197
Cholesteryl cinnamate						
Cholesteryl myristate						
BBBT (5%) and SE-52					Polynuclear aromatic hydrocarbons	53

tion coefficients have been found for various chromatographed substance-liquid-crystalline stationary phase systems²⁰⁵.

By chromatographic methods one can study the character of intermolecular interactions of two-component liquid crystal mixtures⁴⁵ and measure the stability of hydrocarbon-liquid crystal complexes²⁰⁶. It has been shown that a correlation exists between the properties of the smectic mesophase-dissolved substance system found chromatographically and those determined by IR methods¹⁶⁵.

By gas chromatography, making sometimes use of data measured calorimetrically, phase diagrams of liquid crystal-chromatographed substance systems have been determined^{84-87,124,130}. It has been found that the phase diagrams determined solely chromatographically or solely calorimetrically are in agreement⁸⁶. A knowledge of phase diagrams of such systems allow us to draw conclusions about the interaction of the liquid crystal molecules with a chromatographed substance and about the disturbing effect of the latter on the ordering of the liquid-crystalline structure.

The proposal to use gas chromatography for assessing the parameter *S*, *i.e.*, the degree of ordering of the liquid-crystal molecules, seems very interesting. For this purpose the activity coefficient, entropy and enthalpy are used²⁰⁷ or the partial free energy difference¹³⁶ of the substances chromatographed on a liquid-crystalline stationary phase. Such methods are applied to chromatographed substances at infinite dilution but can also be used at finite concentrations.

A new method for measuring the polarity of the substrate surface by applying the principles of chromatography has been proposed. By using this method, the relationship between the liquid-crystal molecular orientation and the polarity of the substrate surface can be elucidated²⁰⁸.

9. SUMMARY

A survey has been made of the properties and applications of liquid-crystalline stationary phases in gas chromatography. In the introduction basic information was given about liquid crystals. The properties of liquid crystals that allow their use as stationary phases were then described. Columns with liquid-crystalline stationary phases are characterized and the temperature dependence of column retention properties is discussed. The relationship between the structure of liquid-crystalline stationary phases and their separating properties is considered. Separations on liquid-crystalline stationary phases have been given a general treatment, and a more detailed list of liquid-crystalline stationary phases and the separations obtained is given.

NOTE ADDED IN PROOF

Recently, various articles on liquid-crystalline stationary phases appeared²⁰⁹⁻²¹².

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