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STRUCTURE OF LIQUID CRYSTAL MOLECULES AND PROPERTIES OF LIQUID-CRYSTALLINE STATIONARY PHASES IN GAS CHROMATOGRAPHY

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SUMMARY

The synthesis is described of four nematic liquid-crystalline stationary phases belonging to the azo and azoxy compound group. The stationary phases obtained were deposited in different amounts on Chromosorb W NAW, which was placed in glass columns (2.1 m × 4 mm I.D.). The temperature dependences of the retention parameters and separation ratios were determined for the particular columns. In addition, the efficiencies of the columns were calculated and separation tests were performed for various mixtures. The results obtained were correlated with the molecular structures of the stationary phases. It was found that azoxy compounds had better separating properties than azo compounds, and liquid crystals with a methyl group were better than those with a cyano group.

INTRODUCTION

Correlation of the properties of a stationary phase with its molecular structure is often difficult with the traditional stationary phases because of an insufficient knowledge of their molecular structure. With liquid crystals the structure of the molecules is precisely defined and therefore one can draw conclusions about its effect on the properties of liquid-crystalline stationary phases. This is of great importance in view of the possibility of synthesizing liquid crystals with properties appropriate for separating specific mixtures. So far this problem has not been given great attention. It has only been found that the molecules of a dissolved substance with a chemical structure similar to that of the liquid crystal are better dissolved and are longer retained in the column¹⁻³. It is also known that, in accordance with predictions based on considerations of the meso-phase structure, molecules of chromatographed sub-

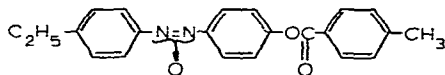
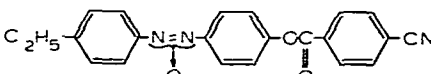
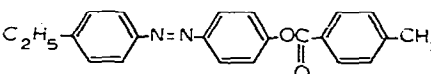
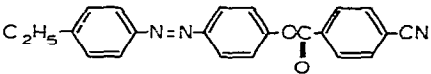
stances with higher length to width ratios are retained longer in the column. In earlier work we also found that the flatter are the molecules of the substances dissolved the longer they are retained in the liquid-crystalline stationary phase⁴. From the studies of Wasik and Chesler⁵ and Martire *et al.*¹, it follows that different liquid crystals have different separation efficiencies with respect to the same mixtures. This has also been confirmed by our studies of the separation of the same disubstituted benzene isomers on different liquid crystals⁶. There is no doubt that, apart from the influence of the molecular structure of chromatographed substances and the structure of the mesophase, the separation efficiency is also substantially affected by the molecular structure of the liquid crystal. In this work we therefore decided to study thoroughly the properties of liquid-crystalline stationary phases of similar general molecular structure when certain elements of that structure are changed.

EXPERIMENTAL

Liquid crystals

We studied four new nematic liquid crystals (I–IV) which were obtained as follows. As substrates we used *p*-ethyl-*p*'-hydroxyazobenzene and toluyl chloride (for compounds I and III) or *p*-cyanbenzoyl chloride (for compounds II and IV) (Table I). In the first step we obtained the azo compound ester, which was subsequently oxidized with peracetic acid. The procedure with compound III was analogous to that described⁷ for *p*-ethyl-*p*'-hydroxyazoxybenzene benzoate. When the esterification was conducted via the Schotten-Bauman reaction⁷, compound IV was obtained in a small yield. A higher yield was obtained when the esterification was conducted in benzene solution in the presence of pyridine according to the procedure described below.

TABLE I
CHARACTERISTIC OF THE STATIONARY PHASES TESTED

| No. | Formula | Phase transition temperatures (°C) |
|-----|---|--|
| I |  | K 97.5 N 250.5 I (directly after crystallization) K 87.5–97.5 N 250.5 I (after melting and cooling) |
| II |  | K 114–115 (beginning of melting) 135–136 N (disappearance of the crystalline phase) > 306 I |
| III |  | K 108 (beginning of melting) 118 N (disappearance of the crystalline phase) 230 I |
| IV |  | K 138 140 N 292 I |

A 45-g amount of *p*-ethyl-*p*'-hydroxyazobenzene, 350 cm³ of benzene and 62 g of anhydrous pyridine were placed in a three-necked flask. With thorough agitation a solution of 34.8 g of *p*-cyanbenzoyl chloride in 150 cm³ of benzene was added gradually and, as a result of the exothermic reaction, the temperature of the solution increased by about 30°. Mixing was continued for a further 2 h, then the flask was left to stand overnight. Next, the flask was emptied into ice-water acidified with hydrochloric acid. The organic layer was separated, washed first with 2% sodium hydroxide solution and then with water, and dried with anhydrous magnesium sulphate. The solution was filtered through silica gel, concentrated to one third of its volume and diluted with methanol, which induced crystallization. We obtained 45 g of *p*-hydroxy-*p*'-ethylazobenzene *p*-cyanobenzoate, which was recrystallized from carbon tetrachloride.

The oxidation of compounds III and IV to the azoxy compounds I and II was carried out as described earlier⁷. The isolated products were recrystallized from acetone-methanol. The purity of compounds I-IV was tested by thin-layer chromatography. The phase transition temperatures of the liquid crystals obtained were determined thermo-optically and are given in Table I.

Both *p*-hydroxy-*p*'-ethylazobenzene *p*-methylbenzoate (III) and *p*-hydroxy-*p*'-ethylazoxybenzene *p*-methylbenzoate (I) show abnormal behaviour when passing from the solid to the nematic state. Compound III, which should have a sharp melting point, unexpectedly melts non-sharply in a manner characteristic of a mixture. Melting begins at 108° but the crystalline phase disappears completely only at 118°. This is not connected with the presence of impurities but may be due to the presence of *cis-trans* isomers.

Compound I, produced by oxidation of III, melted comparatively sharply at 97.5° when crystals obtained from solution were tested. If, however, the crystals were melted and subsequently cooled to the freezing point, on repeated heating there was a distinct phase transition at 87.5°, which is probably connected with a transition in the solid phase. On further heating a transition to the nematic phase is observed at 97.5°. Depending on the conditions, this transition is more or less distinct.

Columns

The liquid crystals were dissolved in methylene chloride and, by evaporation of the solvent, deposited on Chromosorb W NAW of particle size 0.15-0.20 mm used as the support. The amount of liquid crystal deposited on the support was determined by removing it by heating the support at 600° to constant weight. Glass columns 2.1 m long and of 4 mm I.D. were used. Their characteristics are given in Table II.

TABLE II
COLUMNS INVESTIGATED

| | Column No. | | | | | | | |
|---|------------|-----|-----|-----|------|-----|------|-----|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| Stationary phase | I | I | I | II | II | III | III | IV |
| Amount of stationary phase on support (%) | 2.2 | 5.1 | 9.7 | 6.1 | 11.6 | 6.3 | 11.2 | 6.9 |

Apparatus

The investigations were carried by means of a Pye Unicam GCV gas chromatograph provided with a flame-ionization detector (FID). Argon was used as the carrier gas, and its flow-rate was measured with a bubble flowmeter. The temperature of the injector was usually 220° and that of the detector 200°.

Method

Prior to conducting the tests, we heated the columns for 3 h at 200°. After cooling to ambient temperature the columns were heated again, the temperature first being increased in steps of 5°, then 2° finally and 1° in the regions of phase transitions. When the temperature became constant in the column (after about 20 min), we injected 0.1- μ l portions of the tested substance in cyclohexane solution (1:50) with a 1- μ l Hamilton syringe. The dead time was determined using methane. The retention times were measured by means of a stop-watch, the mean being taken of at least two times differing from each other by not more than 0.5 sec.

RESULTS AND DISCUSSION

Dependence of retention parameters on column temperature

For most cases described in the literature, the relationship between the retention time and column temperature, $t'_R = f(t_{col})$, is different for liquid crystals than for traditional stationary phases, and therefore allows one to determine both the melting temperature and the temperature of transition to the isotropic liquid. There are cases, however, where this relationship is similar to those obtained for normal stationary phases^{7,8}.

Fig. 1 shows the variation of the reduced retention time with column temperature for varying amounts of liquid crystal I deposited on the support. When the support is covered with a small amount of liquid crystal (2.2%) the plot is different to that than when the coverage is greater (5.1 or 9.7%). In the first instance the point corresponding to the melting temperature of the liquid crystal is weakly developed. For larger amounts of the liquid crystal these points reach a maximum on the plots, and that maximum is more pronounced when the amount of the deposited liquid crystal is greater. The melting temperatures determined from the plots are different for the particular columns, and for liquid crystal coverages of the support of 2.2, 5.1 and 9.7% these temperatures are 100°, 97° and 90°, respectively. Such a change in the melting temperature is probably related to the interaction with the support which, with small amounts of the liquid crystals, involves all of the molecules of the latter.

The column cooling plots are different from the heating plots. In all instances the retention times increase monotonically during cooling, even if the temperature is lowered below the melting point. This is due to supercooling of the liquid crystal. The supercooled state is stable to temperatures even several dozen degrees below the transition temperature from the solid to the mesophase, and freezing takes place only at these low temperatures.

Fig. 1 supports our earlier conclusion⁹ that the abnormal course of the relationship $t'_R = f(t_{col})$ for the liquid crystal is related to the small amount of the liquid crystal on the surface of the support. In such a situation the bulk phase with the

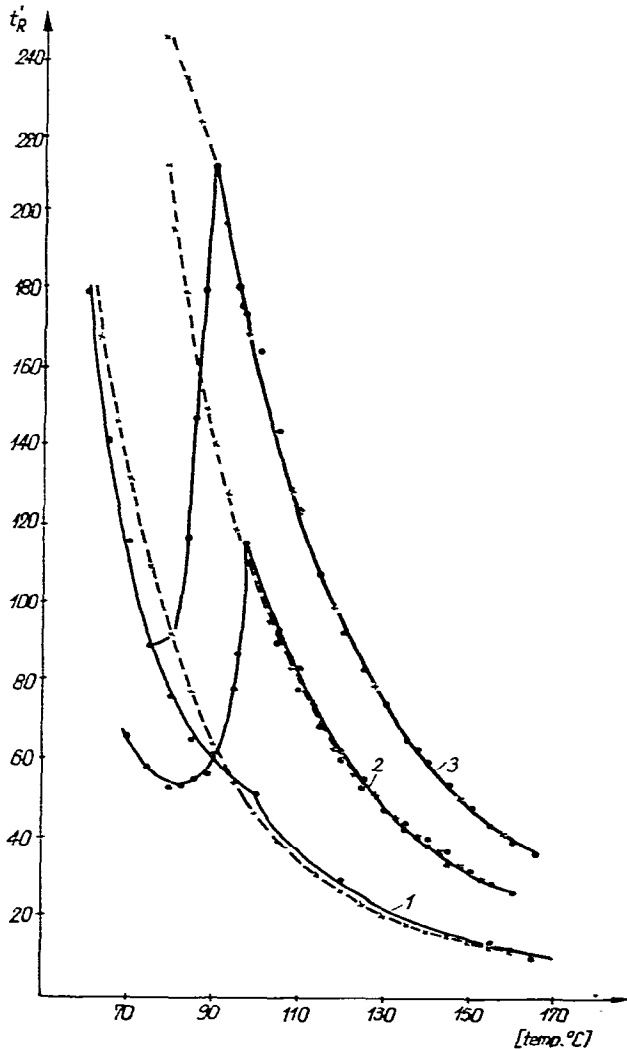


Fig. 1. $t'_R = f(\text{column temperature})$ for *m*-xylene on columns 1-3. Broken lines: cooling of columns.

characteristic liquid-crystalline ordering cannot be formed and therefore the liquid-crystalline phase behaves like a conventional stationary phase. The indistinct extreme observed in Fig. 1 for column 1 may indicate that there are regions on the support where the bulk phase occurs in the form of several layers of the liquid crystal molecules. The forces acting between the support and the liquid crystal molecules may be of different character. These are mainly physical forces but in some instances we cannot exclude the occurrence of chemical bonds.

In Fig. 2, $\log V'_R = f(1000/T)$ plots are presented for columns 3, 5, 7 and 8. The amount of liquid crystal deposited on the support in these columns was such that relationships typical of liquid-crystalline stationary phases were obtained. The columns were not heated to the temperature at which the transition from the mesophase to the isotropic phase occurs, because at temperatures above 200° the liquid crystals bled from the column.

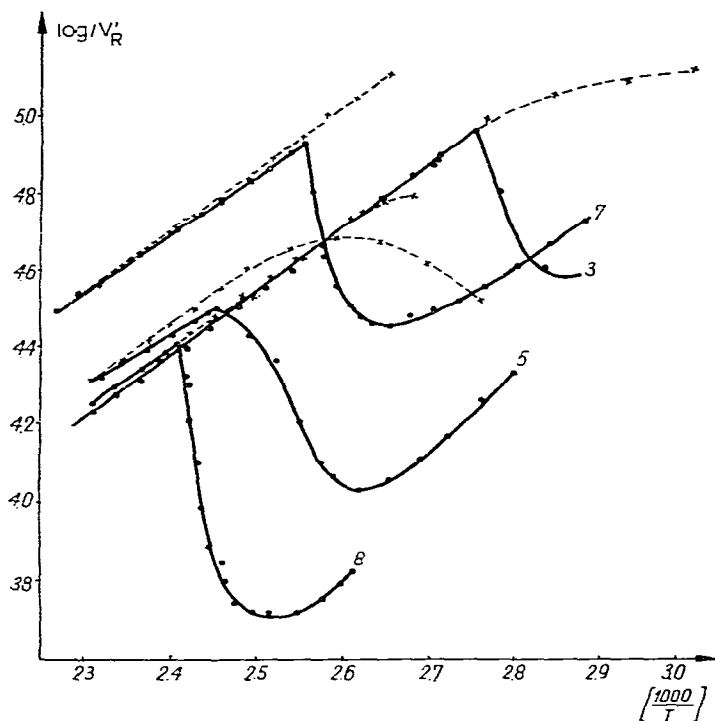


Fig. 2. $\log V'_R = f(1000/T)$ for *m*-xylene on columns 3, 5, 7 and 8. Broken lines: cooling of columns.

Most of the phase transitions observed thermo-optically in the vicinity of the melting temperature were also registered chromatographically.

From Fig. 2 some peculiarities can also be seen. With stationary phase I (column 3) the melting temperature determined chromatographically (90°) corresponds to the phase transition temperature determined thermo-optically after initial melting and cooling to ambient temperature. These conditions are the same as those applied during the chromatographic measurement. The occurrence of some transformations in the liquid crystal during its cooling to temperatures below the melting point is confirmed by the non-linearity of the $\log V'_R = f(1000/T)$ relationship in that region. Only one phase transition was registered chromatographically for that stationary phase, although when thin-layer chromatography was used it was found that it is a mixture of two isomers differing in the position of the oxygen atoms in the azoxy group.

With stationary phase III (column 7) a phase transition was detected at 119° which, as shown by thermo-optical investigations, is related to the complete melting of the liquid crystal. For the same liquid crystal in a smaller amount on the support (column 6), we obtained an additional phase transition at 108° which, on the basis of thermo-optical investigations, was qualified as the beginning of melting (Fig. 3). No contaminants were found in this liquid crystal by thin-layer chromatography.

The beginning and end of melting of liquid crystal II, determined thermo-optically as 114 – 115° and 135 – 136° , respectively, were also found in column 4 (115° and 135°), as can be seen in Fig. 3. In column 5 containing the same liquid crystal

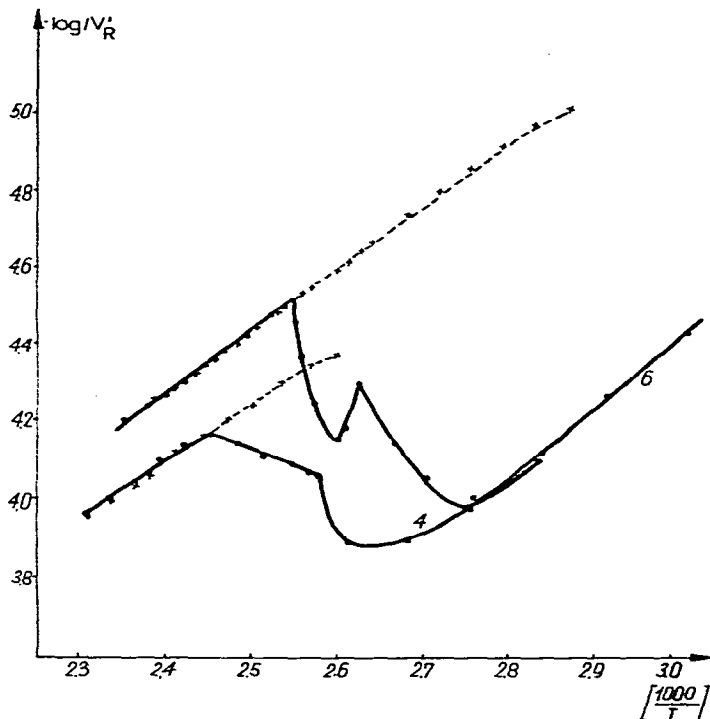


Fig. 3. $\log V'_R = f(1000/T)$ for *m*-xylene on columns 4 and 6. Broken lines: cooling of columns.

only one temperature (135°) from among those found thermo-optically was detected, and it corresponded to the end of melting (Fig. 2).

The melting temperature of phase IV (column 8) determined thermo-optically was $138\text{--}140^\circ$ and that determined chromatographically was 142° .

Variation of the separation ratio with temperature

Figs. 4 and 5 show the separation ratios for *p*- and *m*-xylene (α) obtained in columns 1 and 3 and in columns 4, 6 and 8, respectively. The presence of a greater amount of liquid crystal I on the support causes an increase in the maximum value of α (columns 1 and 3). The value of that maximum for column 2 is intermediate. The separation ratios are usually larger for azoxy than for azo compounds. Also, there is a distinct difference between azo and azoxy compounds as regards the temperature dependence of the separation ratio during cooling of the columns. With azo compounds, cooling of the column produces an increase in the separation ratio over the whole range in which measurements were made. For azoxy compounds the cooling curve obtained is similar to that obtained during heating, with a slight shift of the maximum of the separation ratio towards lower temperatures. This is unexpected as both azo and azoxy compounds are liable to supercooling and it could have been expected that the separation ratios would as a result increase in every case.

The temperatures at which the separation ratios maxima occur in all columns correspond approximately to the melting temperatures of the liquid crystals.

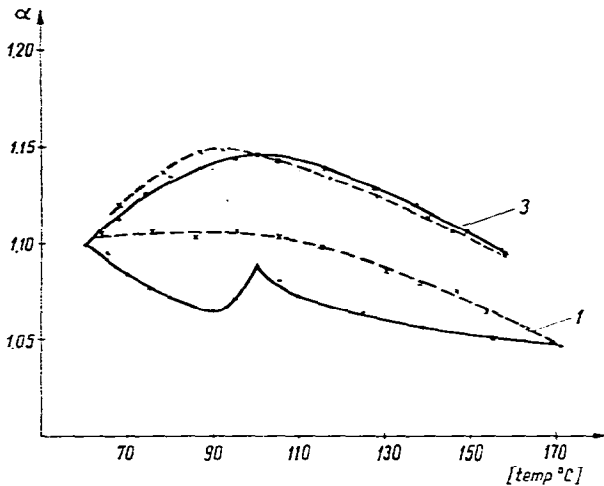


Fig. 4. $\alpha [= t'_R(p\text{-xylene})/t'_R(m\text{-xylene})] = f(\text{column temperature})$ for columns 1 and 3. Broken lines: cooling of column.

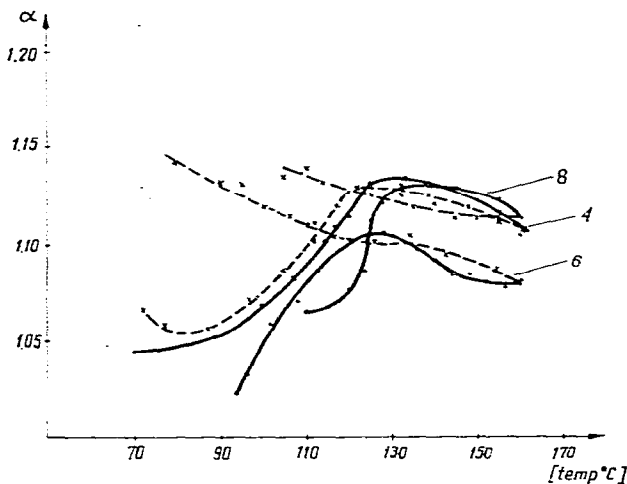


Fig. 5. $\alpha [= t'_R(p\text{-xylene})/t'_R(m\text{-xylene})] = f(\text{column temperature})$ for columns 4, 6 and 8. Broken lines: cooling of column.

Column efficiencies

Figs. 6 and 7 show the efficiencies of columns 1–4 and 6 and 8, respectively, at temperatures corresponding to melting temperatures as determined from the $t'_R = f(t)$ relationship for the retention parameter maxima. The slope of the longer branch of the Van Deemter plot increases with increasing amount of liquid crystal deposited on the support. At the same time, the heights equivalent to a theoretical plate (HETP) increase and the flow velocities (V) of the carrier gas corresponding to the plot minimum decrease from about 22 to about 18 cm³/min. The HETP = $f(V)$ relationships for columns 4 and 8, containing liquid crystals with a cyano group, have flat right-hand branches of the plots, especially for azoxy compounds. A similar resemblance occurs for liquid crystals with a methyl group (columns 2 and 6). In both instances

the azoxy compounds have a lower HETP than the azo compounds. For liquid crystals with a methyl group the difference between the HETP values for azo and azoxy compounds are particularly large. For column 4 (azoxy compound) we obtained 1450 theoretical plates per metre and for column 6 (azo compound) only 550 theoretical plates per metre.

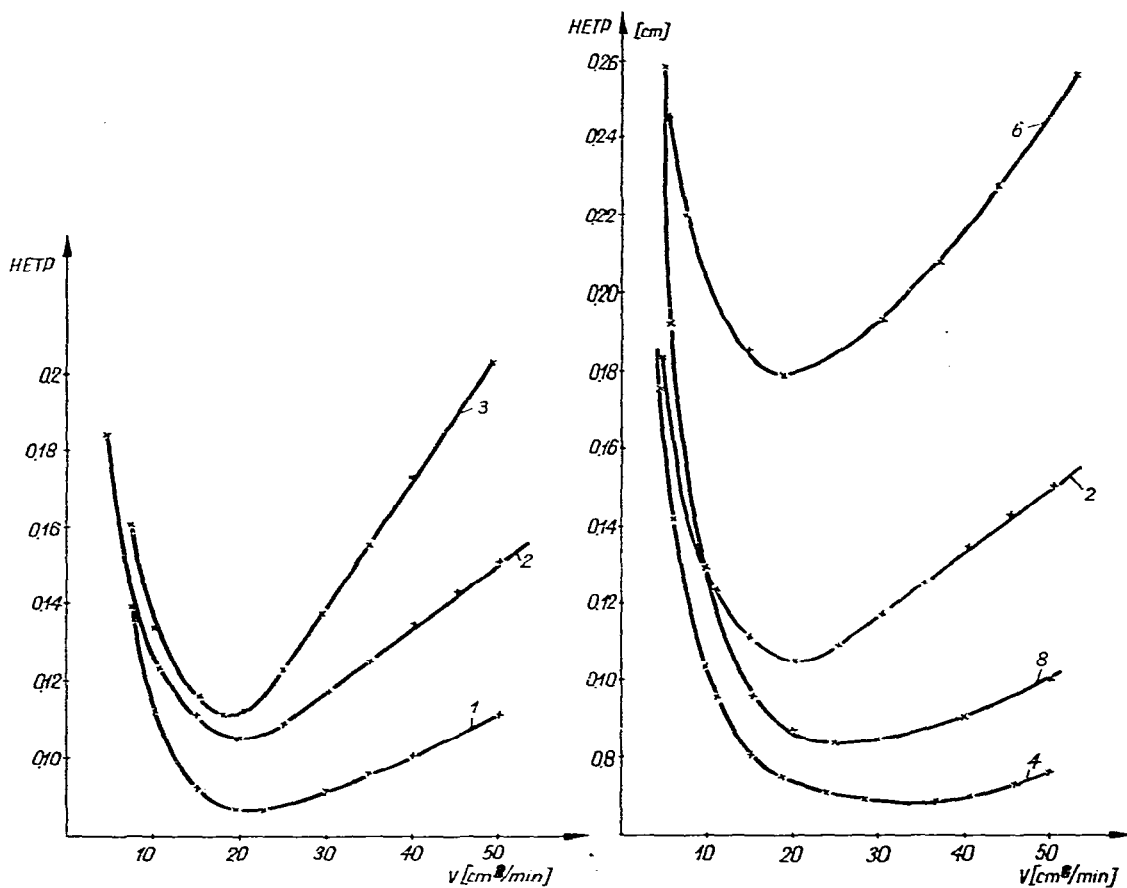


Fig. 6. $HETP = f(V)$ for columns 1-3. Column temperatures: 1 = 100°; 2 = 97°; 3 = 90°. Test substances: column 1, *o*-dichlorobenzene; columns 2 and 3, *p*-chlorotoluene.

Fig. 7. $HETP = f(V)$ for columns 2, 4, 6 and 8. Column temperatures: 2 = 97°; 4 = 120°; 6 = 120°; 8 = 145°. Test substances: column 2, *p*-chlorotoluene; columns 4 and 8, *p*-dibromobenzene; column 6, *p*-dichlorobenzene.

Separations

From the results, it follows that azoxy compounds should have better separating properties than azo compounds towards isomers. Higher separation ratios and lower HETP values were obtained for them.

The separation tests performed confirmed the predictions. With azoxy compounds the separations were better than those with azo compounds. It was also found that the liquid-crystalline stationary phases with a methyl group had better separation properties than those with a cyano group. Separations of various mix-

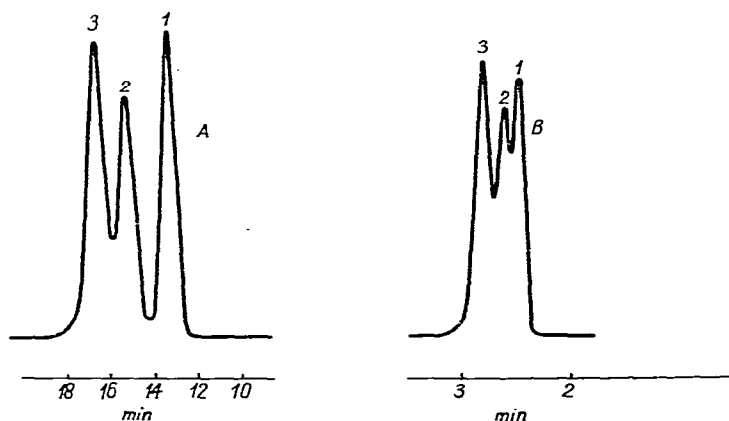


Fig. 8. Types of separation of xylenes on investigated stationary phases. 1 = *m*-Xylene; 2 = *p*-xylene; 3 = *o*-xylene. A: Column 3, temperature of column 70°, argon flow-rate 15 cm³/min. B: Column 4, temperature of column 110°, argon flow-rate 25 cm³/min.

TABLE III
EXAMPLES OF GOOD SEPARATIONS

| Mixture | Time of separation (min) | Temperature of column (°C) | Flow-rate of argon (cm ³ /min) | Column No. |
|--|--------------------------|----------------------------|---|------------|
| Naphthylamines | 28 | 160 | 40 | 4 |
| | 20 | 160 | 40 | 6 |
| Diethylbenzenes | 8 | 90 | 25 | 3 |
| | 18 | 75 | 25 | 6 |
| | 5.5 | 125 | 25 | 8 |
| | 3.5 | 145 | 25 | 8 |
| Chlorotoluenes | 27 | 80 | 15 | 3 |
| Bromotoluenes | 24 | 55 | 25 | 1 |
| Dichlorobenzenes | 9 | 100 | 15 | 4 |
| Chloronitrobenzenes | 31 | 133 | 25 | 4 |
| Cyclohexane, cyclohexene, | 17 | 70 | 15 | 3 |
| benzene, toluene, ethylbenzene, | 15 | 75 | 10 | 6 |
| <i>m</i> -, <i>p</i> - and <i>o</i> -xylenes, propylbenzene | | | | |
| <i>n</i> -Hexane, <i>n</i> -heptane, <i>n</i> -octane, <i>n</i> -nonane, ethylbenzene, <i>m</i> -, <i>p</i> - and <i>o</i> -xylenes, styrene, <i>m</i> -, <i>p</i> - and <i>o</i> -diethylbenzenes | 46 | 70 | 15 | 3 |
| | 9 | 105 | 25 | 8 |
| <i>n</i> -Pentane, <i>n</i> -hexane, <i>n</i> -heptane, <i>n</i> -octane, <i>n</i> -nonane, <i>n</i> -decane | 13 | 70 | 15 | 3 |
| Butyl propionate, butyl valerate, butyl caproate, butyl heptanoate | 10 | 150 | 15 | 3 |
| Ethyl acetate, ethyl propionate, ethyl butyrate, ethyl valerate, ethyl caproate | 9 | 120 | 15 | 3 |
| Propyl acetate, propyl propionate, propyl butyrate, propyl valerate, propyl caproate | 14 | 130 | 15 | 3 |
| 1-Decene, 1-undecene, 1-dodecene, 1-tridecene, 1-tetradecene | 14 | 160 | 15 | 3 |
| Acetone, methyl isobutyl ketone, mesityl oxide, methyl isobutyl carbinol | 6 | 96 | 15 | 3 |
| Benzene, isopropanol, methyl isobutyl ketone | 5 | 96 | 15 | 3 |

tures were studied. Some of them were separated in the supercooled state of the liquid crystals. The stationary phase-support systems revealed a high supercooling stability, and crystallization of the stationary phase took place, for instance in column 1, only at 35°.

The effects of separation depended not only on the kind of liquid crystal but also on its amount on the support. This relationship is presented in Fig. 8, where chromatograms of xylenes are shown. Chromatogram A is characteristic of stationary phases with a methyl group (I and III azo and azoxy compounds). However, when the amount of stationary phase I in the column was small (column 1), chromatogram B was obtained. This chromatogram is characteristic of stationary phases with a cyano group (II and IV azo and azoxy compounds). The chromatograms differ in the ratios of the retention times for the particular isomers. For columns that give chromatograms of type A, $t'_R(o\text{-xylene})/t'_R(p\text{-xylene}) < t'_R(p\text{-xylene})/t'_R(m\text{-xylene})$, and for columns that give chromatograms of type B, $t'_R(o\text{-xylene})/t'_R(p\text{-xylene}) > t'_R(p\text{-xylene})/t'_R(m\text{-xylene})$. It follows that the presence of the methyl or cyano group changes the separating properties of the stationary phases. It seems, however, that the presence of these groups is not the direct cause of the differences observed. Probably the different characters of the two groups (the cyano group is polar) affect differently the arrangement of the molecules on the surface of the support, and this is the reason for the different separations of isomers. This conclusion is confirmed by the behaviour of column 1, where the arrangement of molecules is different to that in the remaining columns with larger amounts of stationary phase I or III, and follows from the different courses of the temperature dependence of the retention parameters as shown in Fig. 1.

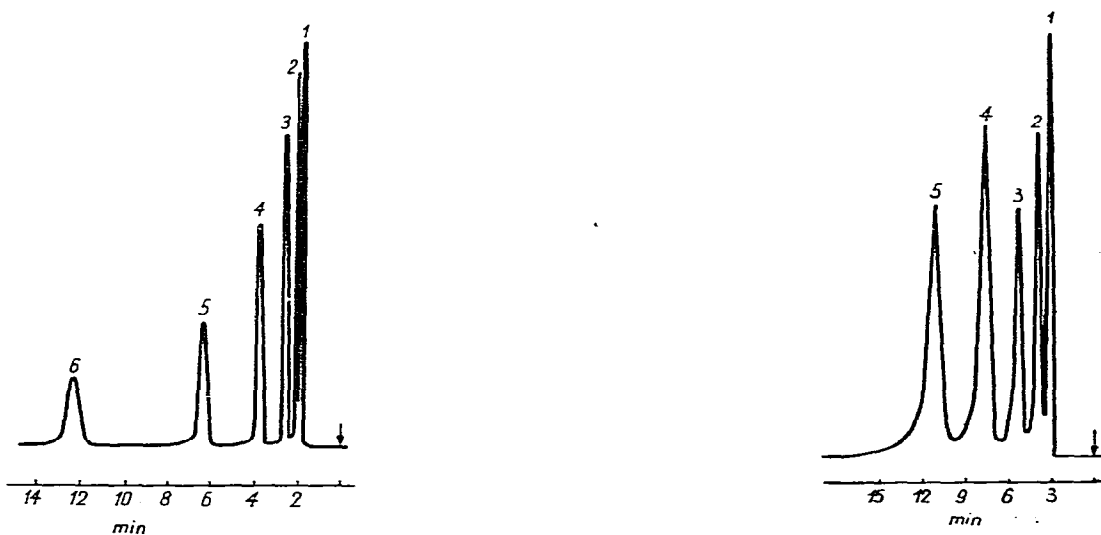


Fig. 9. Separation of saturated hydrocarbons on column 3. Temperature of column 70°, argon flow-rate 15 cm³/min. 1 = *n*-Pentane; 2 = *n*-hexane; 3 = *n*-heptane; 4 = *n*-octane; 5 = *n*-nonane; 6 = *n*-decane.

Fig. 10. Separation of unsaturated hydrocarbons on column 3. Temperature of column 160°, argon flow-rate 20 cm³/min. 1 = 1-Decene; 2 = 1-undecene; 3 = 1-dodecene; 4 = 1-tridecene; 5 = 1-tetradecene.

The examples of separations given in Table III and in Figs. 8–10 confirm the usefulness of the liquid crystals tested (especially I) as stationary phases in gas chromatography.

CONCLUSIONS

The separating properties of the liquid-crystalline stationary phase-support system depend on the structure of the molecule of the liquid crystal, which affects the arrangement of the molecule on the surface of the support. As a result, a change takes place in the relative retention times of the particular components of the mixture and hence the selectivity of the system also changes. Of the stationary phases deposited on Chromosorb W NAW tested, *p*-hydroxy-*p*'-ethylazoxybenzene *p*-methylbenzoate had the best separating properties.

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