CHROM. 11,699

SOME PROPERTIES OF HIGH-TEMPERATURE LIQUID CRYSTALLINE STATIONARY PHASES

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(Received November 22nd, 1978)

SUMMARY

The properties of four high-temperature liquid crystalline stationary phases were compared in order to determine how they are affected by the type of support and the amount of liquid crystal on the support. Retention times were measured and heats of dissolution (adsorption), activity coefficients and relative retention times of test substances were determined as a function of the column temperature. The Van Deemter dependence was determined. It was found that the interaction between the support and the liquid crystal decreases in the order Chromosorb W, Chromosorb W AW, Chromosorb W AW DMCS. Mixtures of high-boiling hydrocarbons and their derivatives were separated. A liquid crystal with naphthalene fragments in its molecule was found to be particularly useful in the separation of naphthalene derivatives.

INTRODUCTION

Liquid crystals are becoming increasingly important as stationary phase in gas chromatography. Their range of applications is increasing and in some countries they are produced specially for chromatographic applications[1].

As yet there are insufficient stationary phases with both good separation properties and the ability to operate at temperatures above 200°. For this reason much recent research has been concentrated on high-temperature liquid crystalline stationary phases, mainly as regards their use in the separation of polycyclic aromatic hydrocarbons and their derivatives. For example, Janini and co-workers have recently published some interesting results[2–5].

High-temperature liquid crystals usually exhibit high molecular weights and low vapour pressures. Therefore, they do not easily bleed out of the column and can be used in temperature programmed work[6]. In comparison with liquid crystals with a narrow range of mesophase, those with a wide range of mesophase usually exhibit better selectivity.

High-temperature liquid crystalline stationary phases make it possible to separate polycyclic aromatic hydrocarbons, naphthalene homologues and their geometric isomers[2–4,7], frequently in nanogram amounts. Thus they are suitable, for

example, for the determination of carcinogens in cigarette smoke[5]. High-temperature liquid crystalline stationary phases have been employed in the separation of isomers of benoxaprofen[8], epimers of steroids[9] and polynuclear azaheterocyclic compounds[10]. By using a high-temperature liquid crystalline stationary phase in the supercooled state. Wasik and Chesler[11] were able to separate some isomers of naphthalene homologues.
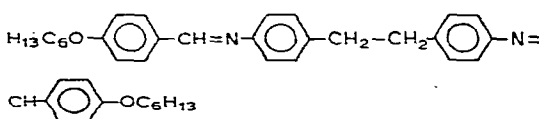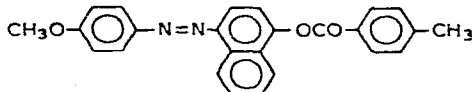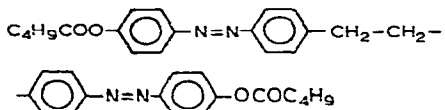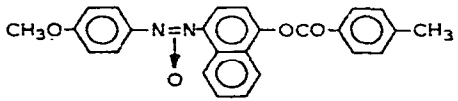
The importance of high-temperature liquid crystalline stationary phases is already considerable and will grow in the future. Hence it is interesting to investigate in detail some properties of liquid crystals with high melting points and a wide range of mesophase deposited on a support and placed in a chromatographic column. In this work we compared the properties of a liquid crystal synthesized by the method of Janini et al.[3] with the properties of three liquid crystals prepared by our method[12].

EXPERIMENTAL

Liquid crystals

The characteristics of the liquid crystals examined are presented in Table I. Compound I (BHxBT), synthesized by the method of Janini et al.[3], has the same melting point and the same transition point to a nematic liquid, its clarification temperature being 2° higher. Compounds II and IV were prepared on the assumption that the naphthalene fragments in their molecules would permit a good separation of isomers of naphthalene derivatives. Liquid crystals II, III and IV have not been investigated previously.

TABLE I

PARAMETERS OF STATIONARY PHASES USED

Phase No.	Formula	Temperature of transition to:		
		Smectic state (°C)	Nematic state (°C)	Isotropic state (°C)
I	$H_{13}C_6O$—⬡—CH=N—⬡—CH_2–CH_2—⬡—N=CH—⬡—OC_6H_{13}	127	229	276
II	CH_3O—⬡—N=N—⬡(naphthalene)—OCO—⬡—CH_3		167	212
III	C_4H_9COO—⬡—N=N—⬡—CH_2–CH_2—⬡—N=N—⬡—$OCOC_4H_9$	165	184	303
IV	CH_3O—⬡—N=N(→O)—⬡(naphthalene)—OCO—⬡—CH_3		182.5	228

Columns

The liquid crystals were deposited on Chromosorb W, Chromosorb W AW and Chromosorb W AW DMCS with particle sizes in the range 0.15–0.20 mm. The deposition of the liquid crystals on supports was performed by evaporating the solvents. The real amount of the stationary phase was determined by removing it from the support at 600°. The glass columns used in this study were 1–2.1 m long with I.D. 4 mm. The characteristics of the columns are given in Table II.

TABLE II

PARAMETERS OF COLUMNS USED

Column No.	Stationary phase	Solvent	Chromosorb	Amount of stationary phase on support (%)	Length of column (m)	Weight of filling (g)
1	I	CHCl$_3$	W	1.16	1	3.76
2	I	CHCl$_3$	W	2.6	1	3.76
3	I	CHCl$_3$	W AW	1.17	2	8.6
4	I	CHCl$_3$	W AW	2.6	2	8.56
5	II	CH$_2$Cl$_2$	W	1.09	1.5	5.63
6	II	CH$_2$Cl$_2$	W	4.11	1.5	5.46
7	II	CH$_2$Cl$_2$	W	5.34	1.5	6.50
8	II	CH$_2$Cl$_2$	W AW DMCS	3.38	1.5	5.35
9	III	CH$_2$Cl$_2$	W	2.03	1	3.94
10	III	CH$_2$Cl$_2$	W AW DMCS	1.93	1.5	5.17
11	III	CH$_2$Cl$_2$	W	4.9	1.5	6.22
12	III	CH$_2$Cl$_2$	W AW DMCS	5.09	1.5	5.78
13	IV	CH$_2$Cl$_2$	W AW DMCS	4.69	1.5	6.92

Apparatus and procedure

A Pye Unicam GCV gas chromatograph equipped with a flame-ionization detector was used. The carrier gas (argon) flow-rate was measured with a bubble flow meter. The columns were heated for 2 h in the thermostat of the apparatus before the study. The heating temperature differed for different columns but was never lower than 200°.

For each column the retention times (t'_R) were measured at different column temperatures. The column was heated, cooled to ambient temperature and then heated gradually again; about 20 min after the temperature had stabilized, the retention times of the test substances were measured with a stop-watch. After each heating cycle the columns were cooled in the same manner. In the region of the phase transition points the changes in temperature were made in steps of 1° or 2°, whereas outside this region the temperature steps were greater. The carrier gas flow-rate was 25 cm^3/min.

The dead time at each temperature was measured using methane. The test substances were 1,3- and 2,3-dimethylnaphthalene (DMN) and α- and β-methylnaphthalene (MN). The second pair was used when the retention times of the DMN were very long. The test substances were dissolved in benzene (1:50) and injected into the column with a 1-mm^3 Hamilton microsyringe.

Column efficiencies at the solid–mesophase transition points were determined for flow-rates in the range 5–50 cm^3/min.

RESULTS AND DISCUSSION

Examples of graphs of retention time *versus* column temperature are shown in Figs. 1 and 2. The amount of the liquid crystal on the support and the type of support used affect these relationships. In some instances they are similar to those observed with conventional stationary phases (*e.g.*, columns 1, 3, 5 and 9), whereas in others they are typical of liquid-crystalline stationary phases (columns 11, 12 and 13). It is a rule that with a small amount of liquid crystal on the support the points corresponding to its phase transitions are not marked or only slightly marked. However, there is no rule that would enable one to anticipate which phase transition will be the first to be marked. For column 1 the first to be marked was the transition from smectic to nematic phase, but for column 9 the first to be marked was the melting point.

The type of support used has a considerable effect on the retention characteristics of the liquid–support system. In general, for the same amount of liquid crystal, the phase transitions are more visible when the following sequence is used: Chromosorb W, Chromosorb W AW and Chromosorb W AW DMCS.
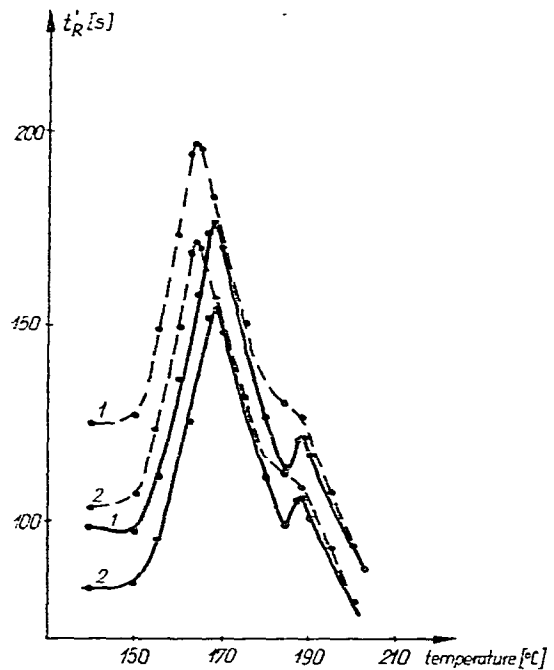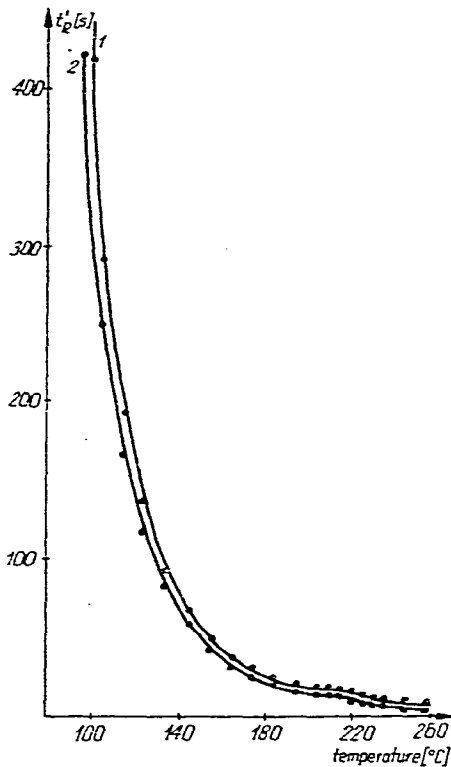

Fig. 1. t'_R *versus* column temperature on column 1. Test substances: 1 = 2,3-dimethylnaphthalene; 2 = 1,3-dimethylnaphthalene.

Fig. 2. t'_R *versus* column temperature on column 12. Test substances: 1 = 2,3-dimethylnaphthalene; 2 = 1,3-dimethylnaphthalene. Broken lines: cooling of column.

The observed retention characteristics are strictly connected with the properties of the liquid crystal–support system and determined by the interaction of the support surface with liquid crystal molecules. When the amount of the liquid crystal on the support is small and the support has a chemically heterogeneous surface all of the molecules are involved in this interaction.

With liquid crystals I, III and IV the phase transitions discussed concern only the melting point and the smectic–nematic transition point. The points of transition to isotropic liquid for these compounds were not determined chromatographically, because they are high and the stationary phases bleed out of the column at lower temperatures.

The measured retention times for compounds I and III are longer during cooling of the column then during heating. With compound II these times are lower for non-silanized supports and almost the same for the silanized supports. With stationary phase III distinct supercooling is observed with both silanized and non-silanized supports, although it amounts to only a few degrees. This is unusual because normally there is either no supercooling or if it is observed it amounts to several tens of degrees.

The heats of dissolution (adsorption) of the test substances in the liquid crystal were determined by using the dependence of the specific retention volume on column temperature[13] (log V_g = f(1000/T)):

$$Q = 19.17 \frac{\log V_g(T_1) - \log V_g(T_2)}{1/T_1 - 1/T_2} \text{ (J/mol)}$$

where V_g is the specific retention volume and T the column temperature (°K). Heats of dissolution (adsorption) for selected columns are presented in Table III.

It can be seen that the heats of dissolution (adsorption) during column heating are higher in the mesophase region then in the solid state or isotropic liquid. During column cooling the heats of dissolution (adsorption) for columns 5–8 are similar to those for isotropic liquids, while for columns 11 and 12 these heats in the corresponding temperature regions are similar to those observed during heating. When the amount of liquid crystal on the support is small and the supports are not silanized the heats of dissolution (adsorption) measured in different columns for the same liquid crystal are in good agreement within each temperature range. With larger amounts of liquid crystal on the support, the measured heats of dissolution (adsorption) are higher. Likewise, the heats of dissolution (adsorption) are higher for Chromosorb W AW DMCS than for the other Chromosorbs.

The heat values given above concern the temperature ranges in which the relationships log V_g = f(1000/T) are linear. No heats of dissolution (adsorption) were determined in regions of phase transitions that exhibit extremes.

The activity coefficients of α- and β-methylnaphthalenes were calculated from the respective specific retention volumes, using the following equation[13]:

$$\gamma = \frac{1.7027 \cdot 10^7}{V_g \, p \, M_L}$$

where V_g is the specific retention volume (cm³/g), p the vapour pressure of the test

TABLE III

HEATS OF DISSOLUTION (ADSORPTION) (Q) OF TEST SUBSTANCES

Column No.	Test substance	Heating of column		Cooling of column	
		Range of temperatures (°C)	Q (J/mol)	Range of temperatures (°C)	Q (J/mol)
5	α- and β-methyl- naphthalene	140–163 163–220	$47.93 \cdot 10^3$ $63.90 \cdot 10^3$	220–140	$49.27 \cdot 10^3$
6	α- and β-methyl- naphthalene	140–170 170–220	$31.94 \cdot 10^3$ $44.67 \cdot 10^3$	220–140	$44.67 \cdot 10^3$
7	α- and β-methyl- naphthalene	140–206 206–220	$47.92 \cdot 10^3$ $47.92 \cdot 10^3$	220–190 190–175 175–140	$47.92 \cdot 10^3$ $23.96 \cdot 10^3$ $47.92 \cdot 10^3$
8	1,3- and 2,3-di- methylnaphthalene	140–165 170–203 210–220	$47.92 \cdot 10^3$ $95.74 \cdot 10^3$ $47.93 \cdot 10^3$	220–210 180–140	$47.93 \cdot 10^3$ $47.93 \cdot 10^3$
9	1,3- and 2,3-di- methylnaphthalene	150–163 165–200	$63.90 \cdot 10^3$ $47.92 \cdot 10^3$		
10	1,3- and 2,3-di- methylnaphthalene	140–160 167–180 184–200	$47.92 \cdot 10^3$ $67.09 \cdot 10^3$ $47.92 \cdot 10^3$		
11	1,3- and 2,3-di- methylnaphthalene	140–150 165–180 187–200	$3.19 \cdot 10^3$ $47.92 \cdot 10^3$ $47.92 \cdot 10^3$	200–187 175–165 150–140	$47.92 \cdot 10^3$ $38.34 \cdot 10^3$ $3.19 \cdot 10^3$
12	1,3- and 2,3-di- methylnaphthalene	170–184 187–200	$63.90 \cdot 10^3$ $38.34 \cdot 10^3$	200–189 180–165	$38.34 \cdot 10^3$ $63.90 \cdot 10^3$

substance (mmHg) and M_L the molecular weight of the stationary phase. The vapour pressure of the test substance can be obtained using Antoine's equation:

$$\log p = A - \frac{B}{C + t_c}$$

where t_c is the column temperature (°C) and A, B and C are coefficients taken from ref. 14.

It was found that the activity coefficients of α- and β-methylnaphthalene increase as the amount of stationary phase on the support decreases. The differences in the activity coefficients of the two substances are small but they increase if there is more liquid crystal on the support. From the point of view of chromatographic separations, the difference in the activity coefficients of components with similar vapour pressures is significant. The activity coefficients of methylnaphthalenes usually differ most in the range of the mesophase during both cooling and heating of the column, but in some liquid crystal–support systems considerable differences were also observed in the range of the mesophase.

The analysis of activity coefficients indicates that larger amounts of liquid crystal on the support and the use of silanized supports should result in better separations. However, the Van Deemter dependence [HETP = f(V)] indicates that column efficiencies increase as the amount of liquid crystal on the support decreases. At the same time, with larger amounts of liquid crystal the graphs become flatter and the optimal carrier gas flow-rate increases. On the other hand, better efficiencies were obtained with silanized Chromosorb, as shown in Fig. 3.
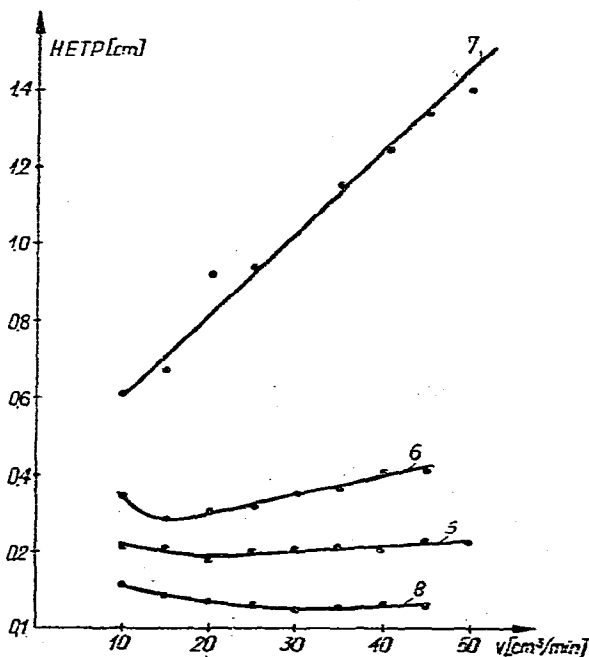
Fig. 3. HETP *versus* flow-rate (*v*) for columns 5–8. Column temperature, 170°; test substances, β-methylnaphthalene for columns 5–7 and 1,3-dimethylnaphthalene for column 8.

A study of the relative retention times ($\alpha = t'_{R_1}/t'_{R_2}$) has proved that this ratio also depends on the amount of liquid crystal on the support. For compound I with Chromosorb W and Chromosorb W AW at about 1% liquid crystal the relative retention times of 1,3- and 2,3-DMN are almost equal in the temperature range 100–230°, with values of 1.1–1.2. When the amount of this compound is increased to *ca.* 2.5%, the relative retention times are highest in the solid-state temperature region, the highest values being noted at lower column temperature. In spite of this, separations in the solid-state temperature region are not useful because of the long time of analysis involved.

For liquid crystal II the relative retention times of α- and β-methylnaphthalene at temperatures from 140 to 220° are nearly equal (1.1–1.15) if the support is not washed with acid. When Chromosorb W AW DMCS is used as the support, the relative retention time of 1,3- and 2,3-DMN decreased from about 1.26 to about 1.14 as the column temperature increased. Cooling of the column results in the same values of relative retention times as during heating.

The relative retention times of 1,3- and 2,3-DMN are unusual for compound III, because they are high within the range of solid state, reach their minimum in the smectic region and begin to increase in the nematic region. This indicates an extremely low separation ability of the smectic mesophase for this pair of isomers. This is illustrated in Fig. 4.

The relationships between the relative retention times of chromatographed substances and the column temperature are different from those observed for low-temperature liquid crystals, for which distinct changes were observed during both the
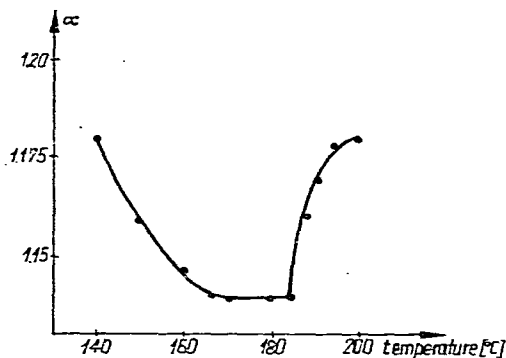
Fig. 4. $\alpha = t_R'(2,3\text{-DMN})/t_R'(1,3\text{-DMN})$ *versus* column temperature for column 12.

solid state–mesophase and the mesophase–isotropic liquid transitions[15]. With high-temperature liquid crystals the transition phase points are sometimes observed but there are no distinct differences in the relative retention times within each temperature range. This may be caused by small differences in "fitting" solutes to the liquid crystal structure within each of its phase regions.

Mixtures of different high-boiling hydrocarbons and their derivatives were separated by using the investigated liquid crystals. Examples of the separations obtained are shown in Figs. 5–9. The separation of the eight-component mixture of naphthalene, methylnaphthalenes and dimethylnaphthalenes was achieved on column 7 using stationary phase II. The results are shown in Fig. 5. A similar separation was obtained using phase I, but 1,4-, 1,5- and 2,3-DMN and 1,3- and 1,6-DMN could not be separated.
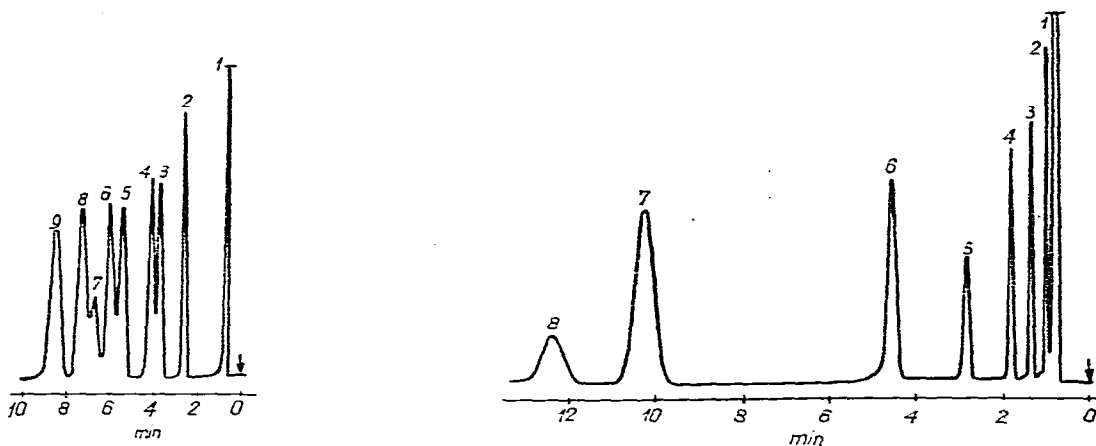

Fig. 5. Separation of isomers of naphthalene on column 7. Temperature, 190°; carrier gas, argon at 25 cm³/min. Peaks: 1 = benzene; 2 = naphthalene, 3 = β-methylnaphthalene; 4 = α-methylnaphthalene; 5,6,7,8 and 9 = 2,6-, 1,3-, 2,3-, 1,2- and 1,8-dimethylnaphthalene, respectively.

Fig. 6. Separation of a mixture on column 12. Temperature, 200°; carrier gas, argon at 25 cm³/min. Peaks: 1 = benzene; 2 = 1,2,4,5-tetramethylbenzene; 3 = naphthalene; 4 = diphenyl ether; 5 = acenaphthene; 6 = benzophenone; 7 = phenanthrene; 8 = anthracene.
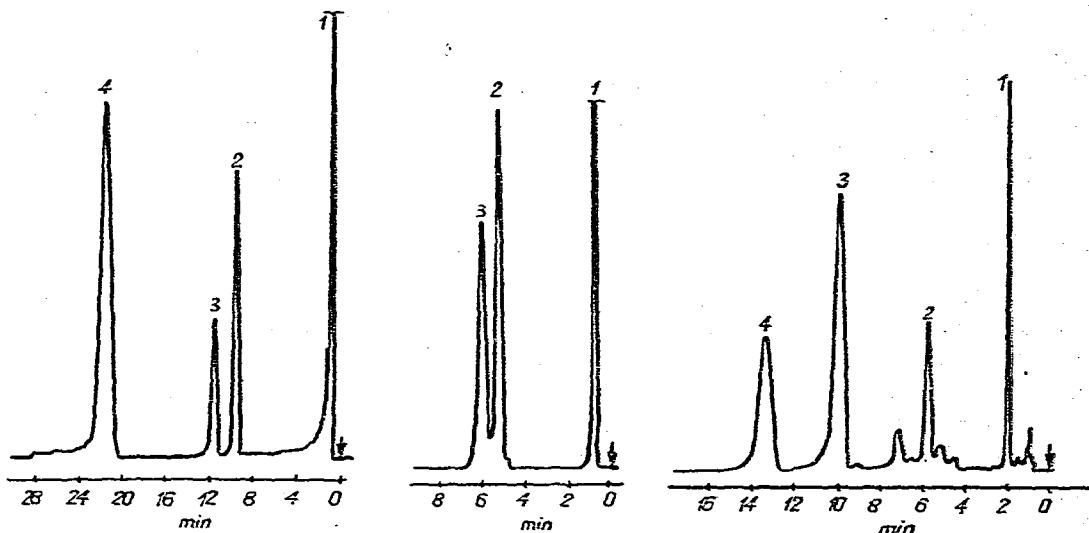
Fig. 7. Separation of a mixture on column 12. Temperature, 200°; carrier gas, argon at 25 cm³/min. Peaks: 1 = dioxane; 2 = phenanthrene; 3 = anthracene; 4 = carbazole.

Fig. 8. Separation of naphthols on column 12. Temperature, 200°; carrier gas, argon at 25 cm³/min. Peaks: 1 = benzene; 2 = 1-naphthol; 3 = 2-naphthol.

Fig. 9. Separation on column 12 of a mixture obtained after synthesis of decylaniline. Temperature, 200°, carrier gas, argon at 25 cm³/min. Peaks: 1 = decylbenzene; 2 = unknown; 3 = decylaniline; 4 = decylacetophenone.

The separations of isomers of methyl derivatives of naphthalene using stationary phase III were much worse than those obtained with phases I and II. Some substances such as 1,3-, 2,3- and 2,6-DMN and α- and β-MN were not separated by using this liquid crystal. Using this phase (III), mixtures of some hydrocarbons were separated and an example is shown in Fig. 6. A good separation of a mixture of anthracene, phenanthrene and carbazole was obtained, as shown in Fig. 7 (column 2). This separation, with important industrial applications, is difficult using either gas–solid or gas–liquid chromatography with conventional stationary phases. Sauerland and Zander[16] were able to separate this mixture on a liquid crystal in 42 min. The separation time achieved on our stationary phase was less then 24 min. Using the same stationary phase, a good separation of α- and β-naphthols (Fig. 8) and a very good separation of naphthylamines were achieved. In the second instance the separation time was less then 44 min, which is better than any time published in the literature[17]. After reaction, mixtures of the semi-products used in the synthesis of liquid crystals, e.g., hexylaniline, octylacetophenone and decylaniline, were also separated on liquid crystal III (Fig. 9).

Most of the substances separated on all of the liquid crystals investigated here were eluted from the column in the same order as their boiling points, which is similar to that observed on conventional non-polar stationary phases. The order of elution of diphenyl and naphthalene from phase I is unusual. Diphenyl is eluted from the column earlier than naphthalene, although their molecular length-to-width ratio (higher for diphenyl) and their boiling points would lead one to expect the reverse order of elution.

The separation properties of stationary phases I and III are similar. They are especially useful in the separation of higher hydrocarbons and their derivatives. Phase II exhibits the best properties in the separation of isomers of naphthalene derivatives. The good and rapid separations obtained on this liquid crystal probably result from the fact that its molecule contains a naphthalene fragment. However, even this liquid crystal did not permit the separation of all of the isomers investigated.

CONCLUSIONS

The retention characteristics of the liquid crystal–support system depend strongly on the properties of the latter, which in turn depend on the type of support used, the character of its surface and the features of the liquid crystal. The particular supports interact in a different manner with the liquid crystal molecules. High-temperature liquid crystals usually have high molecular weights. Thus even with a relatively high coverage of the support with the stationary phase, when the molecules are suitably arranged, the support probably reacts with all of the molecules. This points to the necessity of using a high coverage and thus obtaining retention characteristics with marked phase transitions. However, for analytical purposes such a high coverage of the support with the liquid crystal is not necessary.

The observation made by some workers that substances with molecular structures similar to that of the liquid crystalline stationary phase are separated on the latter better than on a phase with a different molecular structure has been confirmed.

In this work it has been found that among the investigated stationary phases, II and IV are less resistant to high temperatures than I and III.

ACKNOWLEDGEMENTS

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