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## LIQUID CRYSTALLINE CYANOAZOXYBENZENE ALKYL CARBONATES AS STATIONARY PHASES IN SMALL-BORE PACKED MICRO-COLUMNS

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### SUMMARY

Three liquid crystalline cyanoazoxybenzene alkyl carbonates, with hexyl, nonyl or decyl as the alkyl radical, were investigated as stationary phases. They were deposited in various amounts on Polsorb B NAW and on Polsorb B AW and placed in 5 m × 0.8 mm I.D. columns. The retention relationships [ $\log V'_R = f(1000/T)$ ] and column efficiency [HETP =  $f(V)$ ] are connected with the properties of the liquid crystal-support system. The interactions of each of the supports with the liquid crystal differ considerably. For cyanoazoxybenzene hexyl carbonate on Polsorb B AW the efficiency obtained per metre of column length was 6830 theoretical plates. It was found that the variation of the relative retention times of the xylene isomers with column temperature is also dependent on the type of Polsorb used. The liquid crystals investigated have useful properties and can replace successfully the traditional stationary phases used for separating mixtures of various substances.

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### INTRODUCTION

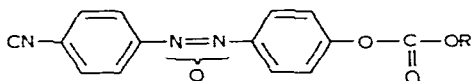
The usefulness of liquid crystals as stationary phases for gas chromatography has been demonstrated by many workers<sup>1-4</sup> and they are established in chromatographic practice<sup>5</sup>. Liquid crystals have been used recently for separating mixtures of isomers<sup>6-12</sup> and polycyclic hydrocarbons<sup>13-16</sup>. So far most investigations have been carried out with the use of common analytical columns several millimetres in diameter, much less often with capillary columns and least often with small-bore packed micro-columns. In earlier work we obtained some results relating to the liquid crystal-support system<sup>17</sup> and separations of some isomers of disubstituted benzenes in small-bore packed micro-columns were achieved<sup>11</sup>. These separations were good,

but some were obtained on relatively long columns (18 m) and the separation times were long. In the present work we decided to investigate the properties of other liquid crystalline stationary phases, *viz.*, cyanoazoxybenzene alkyl carbonates, which so far have not been studied from the standpoint of their application in chromatography. We carried out these investigations in the small-bore packed micro-columns whose properties were described recently by Berezkin *et al.*<sup>18</sup>.

In the investigations of liquid crystalline stationary phases carried out hitherto, little attention was paid to the possibility of their use for purposes similar to those for which traditional stationary phases are applied (not only for separating isomers). We decided, therefore, to ascertain how the liquid crystals investigated will behave with regard to mixtures that contain not only isomers but also some members of homologous series of selected classes of compounds.

## EXPERIMENTAL

We used three liquid crystalline stationary phases of the general formula



where R is hexyl, nonyl or decyl. The preparation of these compounds will be described elsewhere<sup>19</sup>. The characteristics of the liquid-crystalline stationary phases studied are given in Table I.

TABLE I  
PARAMETERS OF STATIONARY PHASES USED

Phase No.	Alkyl radical (R)	Temperature of transition to		
		Smectic state ( $^{\circ}\text{C}$ )	Nematic state ( $^{\circ}\text{C}$ )	Isotropic state ( $^{\circ}\text{C}$ )
I	$\text{C}_6\text{H}_{13}$		73-76	137
II	$\text{C}_9\text{H}_{19}$	61	124	127
III	$\text{C}_{10}\text{H}_{21}$	74		125.5

The liquid crystals were deposited on Polsorb B NAW and Polsorb B AW supports of particle size 0.15–0.20 mm from a methylene dichloride solution. The properties of Polsorb B are similar to those of Chromosorb G<sup>20</sup>.

Polsorb B AW was obtained from Polsorb B NAW by washing with acid according to the method of Hastings *et al.*<sup>21</sup>. After the stationary phases had been deposited on the supports by slow evaporation of the solvent at room temperature, the packing obtained was sieved again and glass columns (5 m  $\times$  0.8 mm I.D.) were filled with the 0.15–0.20-mm fraction. The columns used are specified in Table II.

We used a GCHF 18.3 gas chromatograph, adapted in the Department of Physical Chemistry of the Maria Curie-Skłodowska University for use with small-bore packed micro-columns. The samples were injected into the column through a splitter with a variable splitting ratio; usually a ratio of 1:25 was used. The temperature of the injector was 200 $^{\circ}$  and that of the detector was 160 $^{\circ}$ . The test substances

TABLE II  
COLUMNS USED

<i>Column No.</i>	<i>Stationary phase</i>	<i>Type of Polsorb B*</i>	<i>Concentration of stationary phase on support (%)</i>	<i>Weight of filling in column (g)</i>
1	I	B AW	5.19	1.57
2	I	B AW	2.16	1.58
3	I	B NAW	1.92	1.44
4	I	B NAW	4.85	1.55
5	III	B NAW	1.93	1.41
6	III	B AW	2.13	1.59
7	III	B NAW	4.61	1.55
8	II	B NAW	2.03	1.50
9	II	B AW	2.52	1.35
10	II	B NAW	5.14	1.66

\* AW = acid-washed; NAW = non-acid-washed.

(xylenes and diethylbenzenes) were dissolved in cyclohexane in the ratio 1:50 and injected by means of a 1- $\mu$ l Hamilton syringe. Each column was heated in a thermostat for 2 h at a temperature about 20° higher than that of the liquid crystal transition temperature to the isotropic liquid. At the heating temperature slight bleeding of the stationary phase from the column was observed and in some instances slight yellowing of the packing occurred. After such heating of the columns no further change in colour was observed, nor did the liquid crystal bleed from the column when working at various temperatures, and the reproducibility of the retention parameters was good.

After heating, the column was first cooled to ambient temperature and subsequently heated by gradually increasing the temperature, controlled by means of a thermometer to  $\pm 0.2^\circ$ . At every temperature the column was heated for 15 min when the dead time was determined using methane. The retention times of the test substances were measured by means of a stop-watch. The results were considered to be good when in two successive measurements they did not differ by more than 0.5 sec.

The efficiency of the column was tested at temperatures corresponding to the maximal retention time; these temperatures were approximately the melting points. When no such maximum existed, the column efficiency was measured at the melting point of the liquid crystal as determined by the thermo-optical method. In some instances the relationship between the HETP and the column temperature was also examined.

## RESULTS AND DISCUSSION

Considerable differences were observed in the behaviour of Polsorb B AW and Polsorb B NAW with respect to the liquid crystalline stationary phases examined. For compounds II and III on Polsorb B NAW the relationship  $\log V'_R = f(1000/T)$  was similar to that for the traditional stationary phases both at about 2% and 5% coverage of the support with these compounds. With Polsorb B AW this relationship is typical of liquid crystals with distinct phase transition tem-

peratures (Figs. 1 and 2) at about 2% coverage of the support. It is interesting that for compound I no such differences were observed with the different supports. In the latter instance the effect of the support is only that the difference between the minimum in the solid and the maximum corresponding to the melting point on the  $\log V'_R = f(1000/T)$  plot is greater for Polsorb B AW than for Polsorb B NAW (Fig. 3). The different pattern of the retention relationships for compound I is probably the result of this compound having a molecular structure that differs from those of compounds II and III as regards the structure of the meso-phase. Compound I has a nematic structure whereas compound II in the major part of the meso-phase has a smectic structure (it has a nematic structure only over the range of 3°), and compound III has a smectic structure only.

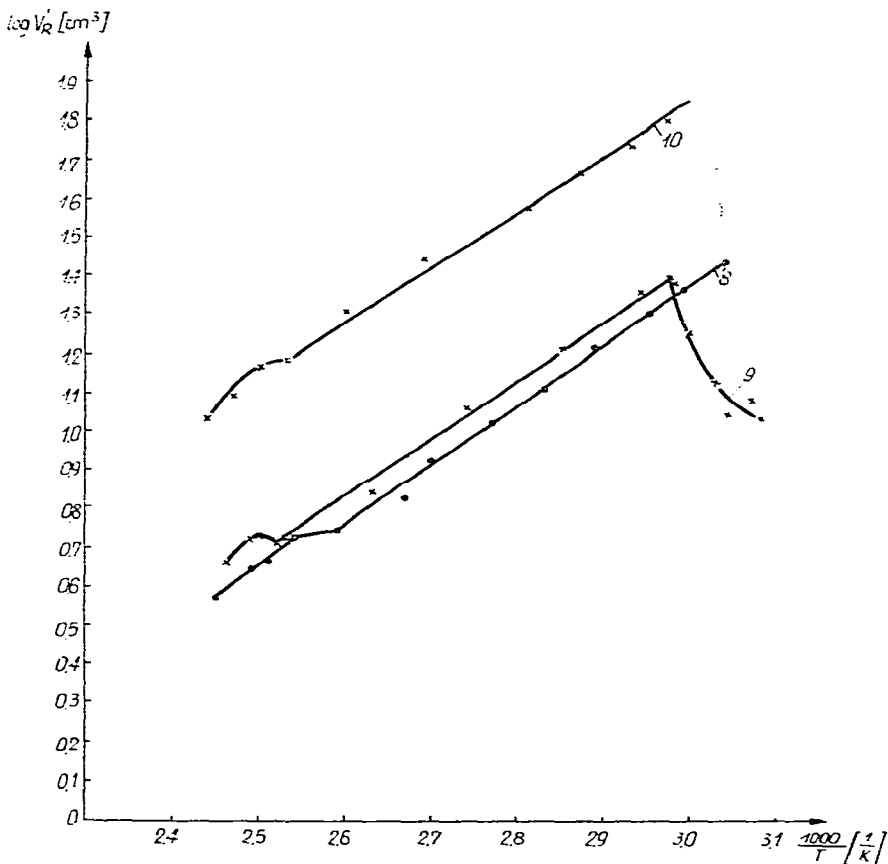


Fig. 1. Curves of  $\log V'_R = f(1000/T)$  for columns 8-10; flow-rate of nitrogen, 2.5 cm<sup>3</sup>/min; test substance, *m*-xylene.

From the above, it follows that one or other type of retention characteristic, probably related to the interaction of the liquid crystal molecules with the support, is dependent not only on the condition of the support surface and the properties of the liquid crystal separately, but also on both of these parameters simultaneously, *i.e.*, on the features of the whole liquid crystal-support system. Depending on the

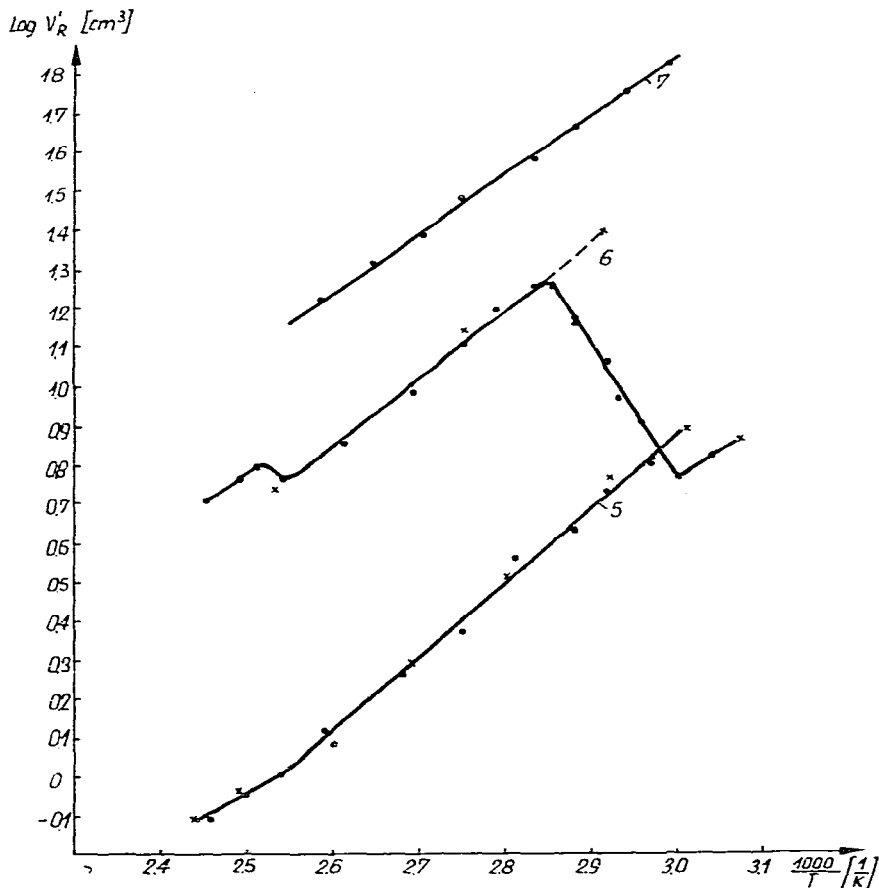


Fig. 2. Curves of  $\log V'_R = f(1000/T)$  for columns 5-7; flow-rate of nitrogen, 2.5  $\text{cm}^3/\text{min}$ ; test substance, *m*-xylene.

properties of the system, that is, on the mutual interactions, the molecules of the liquid crystal in different situations on the surface of the support and therefore react differently with the substances being chromatographed. It seems that this applies firstly to temperatures in the zone of phase transitions, as in the range corresponding to the meso-phase the plots representing the relationship  $V'_R = f(1000/T)$  are approximately parallel. The greatest differences in the retention relationships occur, however, in the region where the liquid crystal in the bulk is a solid. The occurrence of such large differences in the retention parameters for this temperature range, depending on the properties of the liquid crystal-support system, is difficult to explain. The interaction of the liquid crystal with the support giving a retention characteristic typical of a traditional stationary phase usually occurs at low support coverages, but in some instances also at high coverages<sup>22,23</sup>. It seems that the occurrence of a layer of adequate thickness on the support surface is a necessary condition for obtaining a retention characteristic that enables one to determine the phase transitions of the liquid crystal. The layer should contain such a number of molecules that ordering forces in the liquid crystal be not dominated by the surface

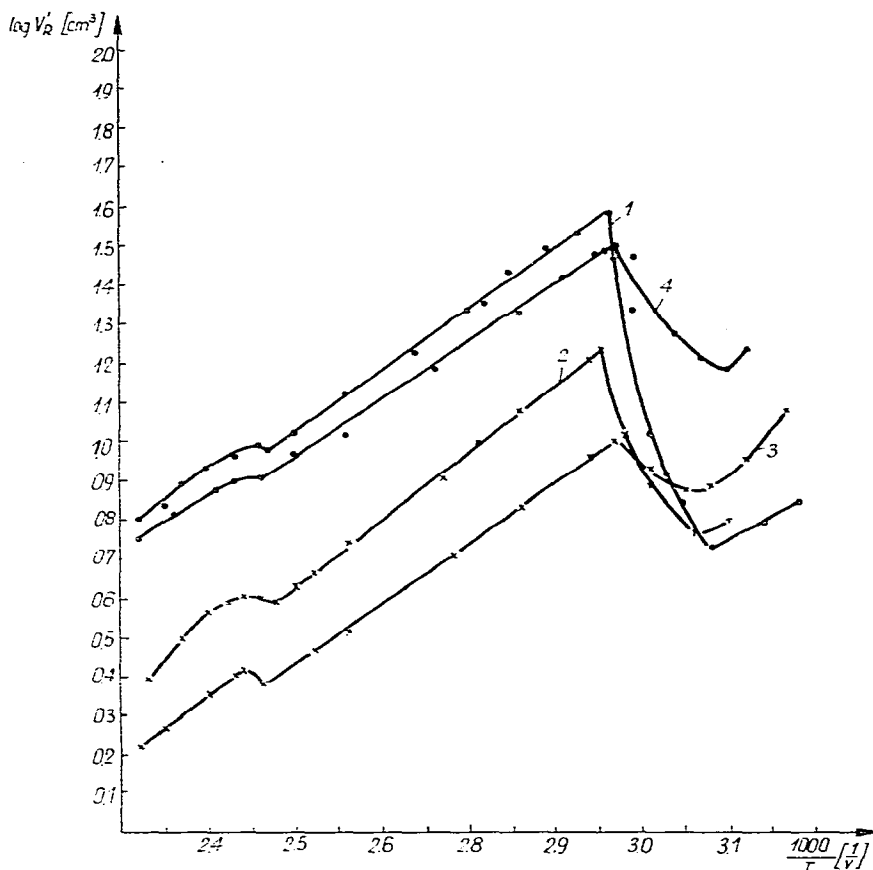


Fig. 3. Curves of  $\log V'_R = f(1000/T)$  for columns 1-4; flow-rate of nitrogen, 2.5  $\text{cm}^3/\text{min}$ ; test substance, *m*-xylene.

forces of the support. Perhaps the thickness of the layers is so great that drops form, which would be in agreement with the drop model of the distribution of the stationary phase on the support accepted by many workers<sup>24</sup>.

The retention times of test substances increase with increasing amount of liquid crystal on a particular support. When the amounts of a given liquid crystal are similar, the retention times are higher for Porsorb B AW than for Porsorb B NAW in every instance.

The effect of different features of Porsorb B NAW and Porsorb B AW on the properties of the liquid crystal-support system is also revealed in the column efficiency characteristics [ $\text{HETP} = f(V)$ ]. For the nematic compound I and the smectic compound III, higher efficiencies were obtained on Porsorb B AW (Figs. 4 and 5). For the smectic-nematic compound II, higher efficiencies were obtained for Porsorb B NAW (Fig. 6). The efficiencies of columns with the nematic compound I (irrespective of the support used) are much higher than those with compounds II and III (Figs. 4-6).

The efficiency obtained for column 1 was 6830 theoretical plates per metre at a flow-rate  $V = 1.2 \text{ cm}^3/\text{min}$ , and for column 9 it was only 420 theoretical plates

HETP[mm]

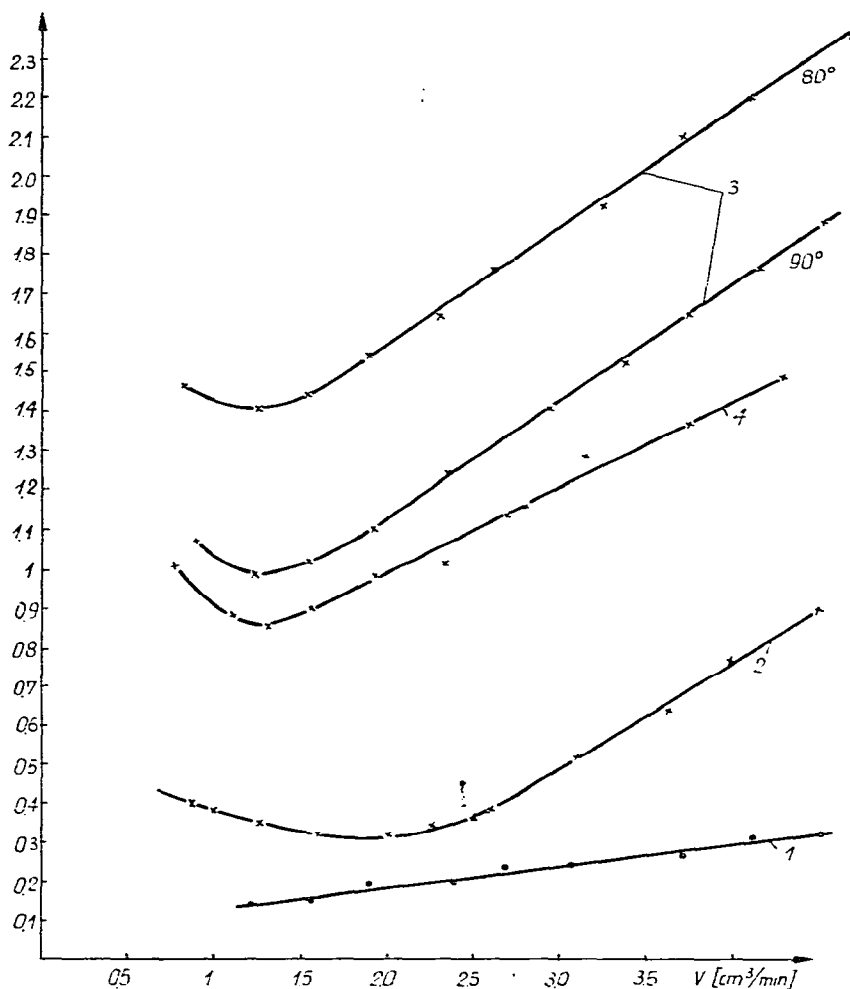


Fig. 4. HETP versus flow-rate ( $V$ ) for columns 1-4. Column temperature,  $80^\circ$ ; for column 3, additional temperature  $90^\circ$ ; test substance, *m*-xylene.

per metre at  $V = 0.8 \text{ cm}^3/\text{min}$ . The high efficiencies of columns with compound I as the stationary phase are probably related to the nematic structure of its mesophase. For compound I it was also found that the dependence of HETP on the flow-rate of the carrier gas is small, which is a characteristic feature of small-bore packed micro-columns. A larger amount of the stationary phase in the column results in a decreased slope of the right-hand branch of the Van Deemter plot (Fig. 4). A smaller slope of that branch was usually observed on changing from a traditional to a small-bore packed micro-column with the same packing. Many workers relate this finding to the better packing of the latter columns. We have now found a similar relationship for small-bore packed micro-columns when the amount of the stationary phase on the support increases.

In Figs. 4 and 6 the effect of temperature on the  $\text{HETP} = f(V)$  relationship

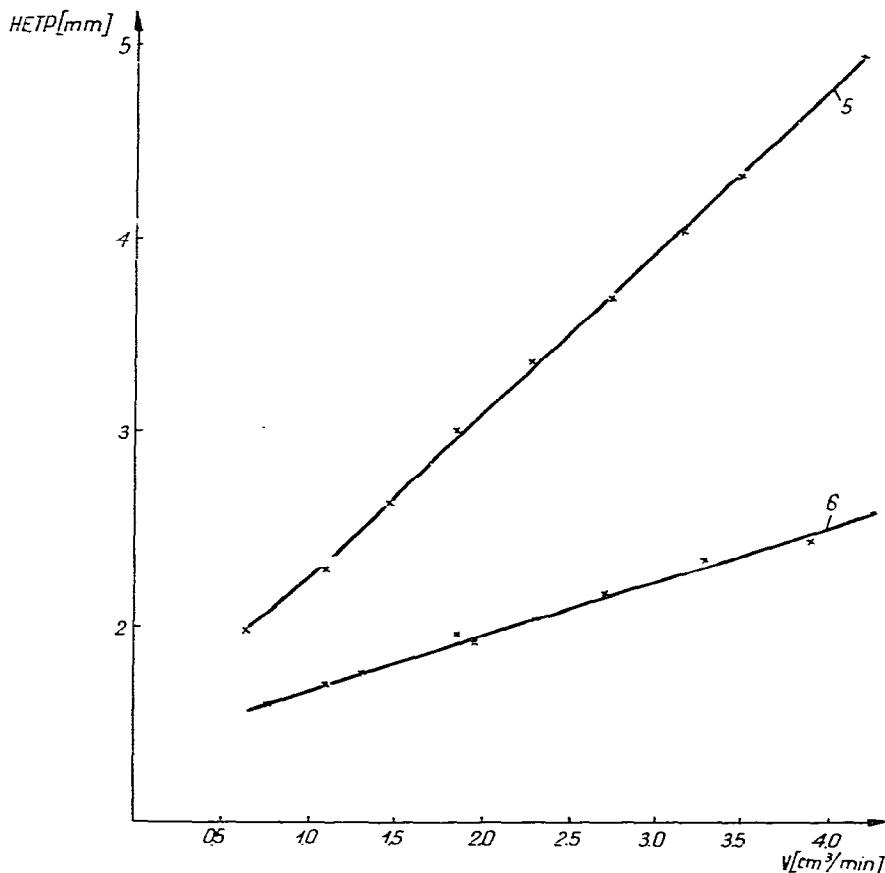


Fig. 5. HETP versus flow-rate ( $V$ ) for columns 5 and 6. Column temperature, 80°; test substance, *p*-diethylbenzene for column 5 and *m*-xylene for column 6.

is also shown. In both instances an increase in the column temperature causes an increase in the efficiency, which is probably due to the lower viscosity of the liquid crystal and the related decrease in the mass transfer resistance. The effect of temperature on the column efficiency in the range including the solid, mesophase and isotropic liquid is presented in Fig. 7 for compound I.

In the temperature range corresponding approximately to the mesophase range the column efficiency increases, first rapidly and then slowly. For the solid and isotropic liquid an increase in temperature results in a decrease in column efficiency. It follows that it would be advantageous to use such a column at temperatures corresponding to the upper range of the mesophase. With liquid crystalline stationary phases, account should also be taken of the separation ratio, which, being related to the degree of ordering ( $S$ ) of the liquid crystal molecules on the support, has a maximum at temperatures different from those at which the maximal column efficiency occurs. The separation ratio reflects the column selectivity towards substances that are difficult to separate.

Fig. 8 shows the relationship  $\alpha = f$  (column temperature) where  $\alpha = t'_R$  (*p*-xylene);  $t'_R$  (*m*-xylene) for compound I deposited in an amount of about 2% on



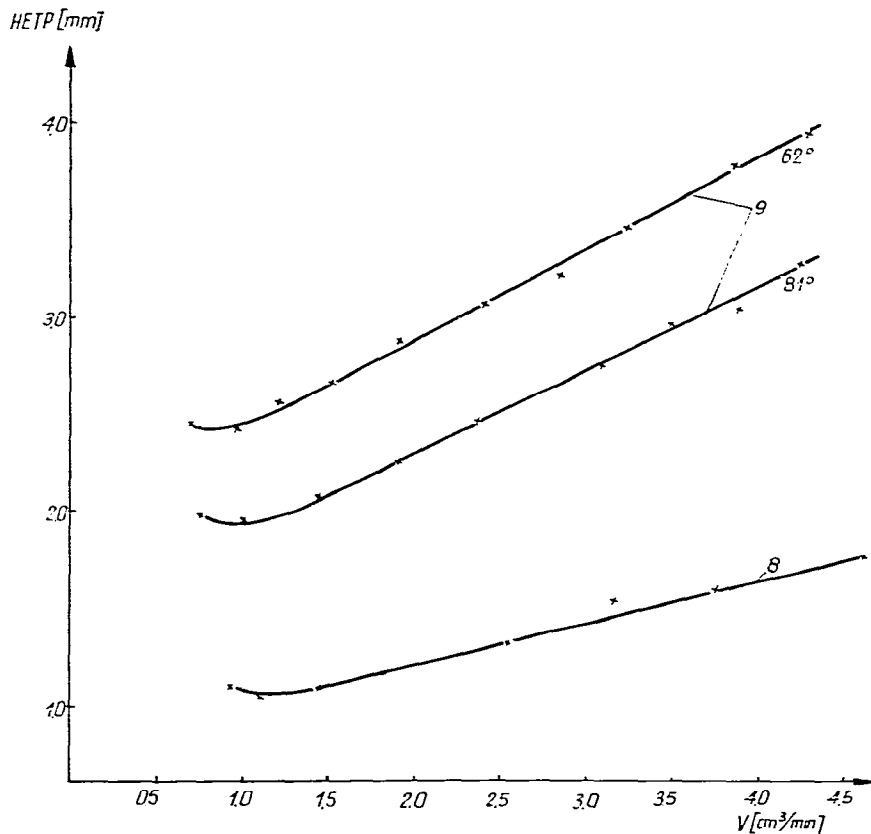


Fig. 6. HETP versus flow-rate ( $V$ ) for columns 8 and 9. Column temperature,  $62^{\circ}$ ; for column 9, additional temperature  $81^{\circ}$ ; test substance, *m*-xylene for column 8 and *p*-diethylbenzene for column 9.

Polsorb B AW (column 2) and Polsorb B NAW (column 3). For columns 1 and 4, the shapes of the above relationship were the same as those for columns 2 and 3, respectively. Here we also observe a difference due to the influence of the two types of support. For acid-washed Polsorb the maximum of  $\alpha$  appears at a column temperature higher than that for Polsorb that has not been acid washed, but the maximum is higher for the latter (1.08) than for the former (1.05). In both instances the maximum of  $\alpha$  appears near the melting point of the liquid crystal. For compounds II and III the temperature at which  $\alpha$  is at a maximum is lower for Polsorb B AW than for Polsorb B NAW.

The value of  $\alpha$  for *m*- and *p*-xylene at the transition temperature to the isotropic liquid is usually greater than unity, but at a temperature several degrees higher it assumes a value of unity or even less.

In Fig. 8 it can be seen that the value of  $\alpha$  varies considerably in the solid temperature range, depending on the type of support. This confirms the observation that differences in the liquid crystal-support interactions also occur at temperatures corresponding to the solid state of the liquid crystal, which has already been found for the retention relationships.

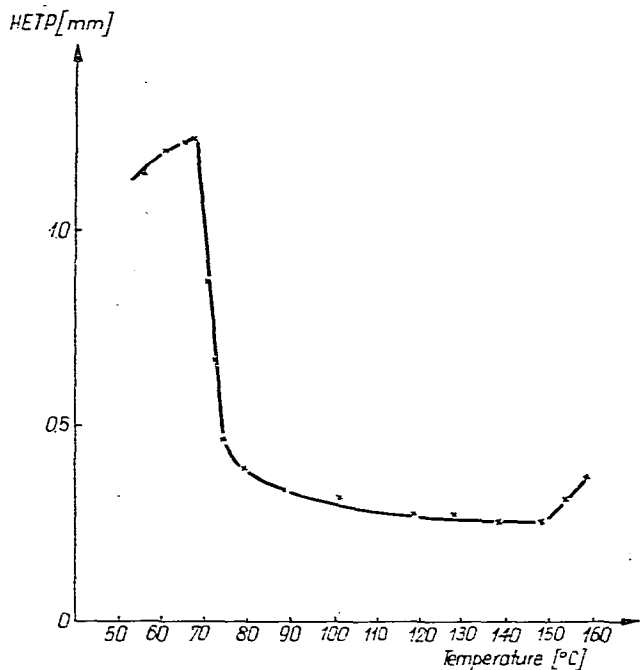


Fig. 7. HETP versus temperature of column 2. Flow-rate of nitrogen, 2.5 cm<sup>3</sup>/min; test substance, *m*-xylene.

In Table III the maxima of the relative retention times for xylene isomers are given.

The liquid crystals investigated show good separation properties towards various classes of compounds. In some instances, however, good separation was achieved at temperatures much greater than the temperatures corresponding to the maximum of  $\alpha$ , even at temperatures higher than the isotropic liquid transition tem-

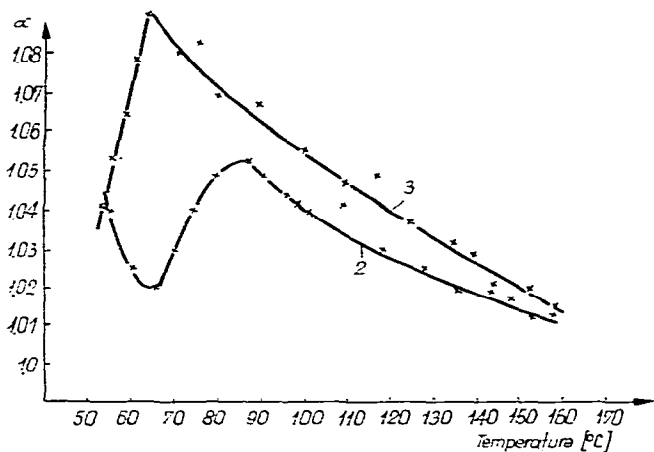


Fig. 8.  $\alpha [t'_R(p\text{-xylene})/t'_R(m\text{-xylene})]$  versus temperature of columns 2 and 3.

TABLE III  
MAXIMAL RELATIVE RETENTION TIMES FOR XYLENE ISOMERS

Column No.	Temperature of column ( $^{\circ}$ C)	$\alpha_{max.}$		
		<i>p</i> -/ <i>m</i> -Xylene	<i>o</i> -/ <i>m</i> -Xylene	<i>o</i> -/ <i>p</i> -Xylene
1	76	1.05	—	—
2	86	1.05	—	—
3	64	1.08	—	—
4	66	1.07	—	—
5	95	1.02	1.225	1.20
6	74	1.045	1.27	1.22
8	73	1.045	1.27	1.22
9	50	1.045	1.23	1.18
10	60	1.03	—	—

perature. This applies especially to separations for which a high column selectivity is not required. Examples of good separations are given in Table IV.

For preparing the mixtures we used chemically pure substances manufactured by various companies. With acetates and ethers more components were detected than were used for preparing the mixture, owing to the high selectivity of the liquid crystalline stationary phases revealing the presence of contaminants in some of the substances used. Under optimal conditions of column operation seven impurities were detected (in very small amounts) in the cyclohexane used for dissolving the test substances. The separations of alcohols were inferior to those obtained for other groups of compounds, both polar and non-polar.

The separations considered did not require supercooling of the liquid crystals, although such a treatment is possible and might be useful in some separations.

## CONCLUSIONS

The alkyl cyanoazoxybenzene carbonates investigated proved to be better as stationary phases than the liquid crystals described earlier<sup>11,17</sup>. Of the stationary phases tested, phase I had the best properties. When it was used, good separations of xylene and ethyltoluene isomers were obtained in 15 and 18 min, respectively, on columns 5 m long (column 1).

It can be inferred from the results that liquid crystals can replace some traditional stationary phases. Their properties are the same as those of the traditional stationary phases as regards the separation of the members of a homologous series. They can operate over a wide range of temperatures and the analysis times are short. In addition, the liquid crystalline stationary phases have a high selectivity at lower mesophase temperatures and can be utilized for separating mixtures that are difficult to separate on traditional stationary phases, *e.g.*, geometric isomers.

The small-bore packed micro-columns used were very stable in operation. Although no detailed investigations were made, the columns did not change their properties, gave reproducible results and the column packing did not degenerate.

TABLE IV  
EXAMPLES OF SEPARATIONS OBTAINED ON DIFFERENT COLUMNS

<i>Good separation of mixture</i>	<i>Column No.</i>	<i>Temperature of column (<math>^{\circ}</math>C)</i>	<i>Flow-rate of nitrogen (<math>\text{cm}^3/\text{min}</math>)</i>	<i>Time of separation (min)</i>
C <sub>5</sub> -C <sub>9</sub> alkanes	1	80	4.5	5
	2	79	4.5	3
	6	110	2.5	3.5
	8	64	2.5	7
	8	88	2.5	4
C <sub>5</sub> -C <sub>10</sub> alkanes	4	75	2.5	12
C <sub>6</sub> -C <sub>14</sub> alkanes	2	159	2.5	6.5
	4	139	2.5	8
	6	135	2.5	11
C <sub>6</sub> , C <sub>8</sub> , C <sub>9</sub> , C <sub>10</sub> alkenes	6	110	2.5	6
C <sub>6</sub> , C <sub>8</sub> , C <sub>9</sub> , C <sub>10</sub> , C <sub>12</sub> alkenes	4	139	2.5	5
C <sub>5</sub> -C <sub>7</sub> cycloalkanes	1	80	4.5	4
	2	79	4.5	2.5
	8	88	2.5	3
	8	57	2.5	5
Cyclohexane, cyclohexene, benzene	1	157	2.5	2.5
Acetates (methyl, ethyl, <i>n</i> -propyl, <i>n</i> -butyl)	4	139	2.5	3
	8	88	2.5	4
Ethers (diethyl, di- <i>n</i> -butyl, di- <i>n</i> -amyl, diisoamyl, butyl glycydyl)	8	125	2.5	26
Ethylbenzene, <i>m</i> -, <i>p</i> - and <i>o</i> -xylene	1	79	4.5	15
<i>n</i> -Hexane, trichloromethane, carbon tetrachloride, benzene	1	80	4.5	3.5
Trichloromethane, carbon tetrachloride, trichloromethane, dichloroethane	4	75	1.9	6.5
Dichloromethane, carbon tetrachloride, trichloromethane, dichloroethane, tetrachloroethane, chlorobenzene, <i>o</i> -dichlorobenzene, <i>p</i> -chlorotoluene, 1,2,4-trichlorobenzene	4	88	2.5	45
<i>n</i> -Hexane, <i>n</i> -heptane, <i>n</i> -octane, benzene, <i>n</i> -nonane, toluene, <i>n</i> -decane, ethylbenzene, <i>m</i> -, <i>p</i> - and <i>o</i> -xylene, propylbenzene, styrene, <i>m</i> -, <i>p</i> - and <i>o</i> -ethyltoluene	4	75	2.5	30
Cyclohexane, cyclohexene, benzene, toluene, ethylbenzene, <i>m</i> -, <i>p</i> - and <i>o</i> -xylene, <i>m</i> -, <i>p</i> - and <i>o</i> -ethyltoluenes	1	80	4.5	15
	1	80	1.8	25
	1	80	1.3	30

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