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PROPERTIES OF LIQUID CRYSTALLINE CYANOAZOXYBENZENE ALKYL CARBONATES AS STATIONARY PHASES IN GAS CHROMATOGRAPHY

ZYGFRYD WITKIEWICZ*, JAROSŁAW SZULC, ROMAN DĄBROWSKI and JANUSZ SADOWSKI

Institute of Chemistry, Military Technical Academy, 01-489 Warsaw 49 (Poland)

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SUMMARY

Seven liquid crystalline azoxybenzene *p*-cyano-*p'*-alkyl carbonates have been tested as stationary phases, using Chromosorb W as the support and xylene isomers as the solutes. The data obtained on the effect of the properties of the liquid crystal-support system on column selectivity and efficiency were utilized in the separation of mixtures of disubstituted benzene isomers.

INTRODUCTION

Systematic studies of azo and azoxy compounds as liquid-crystalline stationary phases have shown that their cyanoalkoxy and cyanoalkyl carbonate derivatives give good separations of disubstituted benzene isomers¹⁻⁶. Among these stationary phases, the mixtures of isomers of azoxybenzene *p*-cyano-*p'*-alkyl carbonates show the best separation properties⁴⁻⁶.

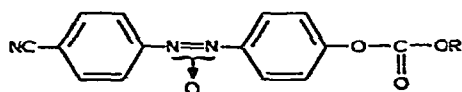
In the present work we study in greater detail the properties of azoxybenzene cyanoalkyl carbonates using seven compounds, four of which have not so far been used in gas chromatography (GC).

The properties of the support-stationary phase-solute system are characterized in terms of retention values, separation ratios, activity coefficients and dissolution (sorption) heats. The effects of the support used and amount of the liquid-crystalline stationary phase deposited on the support on the retention characteristics have been studied for xylene isomers. We also investigated whether the differences in the interaction of the supports with the liquid-crystalline stationary phases can be detected by means of electron microscopy. A further aim of the work was to ascertain how the physicochemical properties of the liquid crystal-support systems affect their separation properties.

EXPERIMENTAL

Liquid-crystalline stationary phases

Azoxy compounds of the general formula



were prepared in our laboratory. The nature of the alkyl group, R, and the phase transition temperatures, determined by thermo-optical methods, are summarized in Table I. The phases C_{5a} , C_7 and C_{12} have not so far been investigated as stationary phases; C_5 , a mixture of isomers containing about 90% of the higher melting isomer, was also studied for the first time. However, a mixture of isomers of compound C_5 very close to that of the eutectic has been tested^{3,5}. The phases C_6 and C_{10} have been investigated in small-bore packed micro-columns using Polsorbs as supports⁶.

TABLE I
LIQUID-CRYSTALLINE STATIONARY PHASES

Phase	Alkyl group	Comments	Temperature ($^{\circ}$ C) of transition to			
			Smectic liquid	Nematic liquid	Cholesteric liquid	Isotropic liquid
C_{5a}	$-\text{CH}_2-\underset{\text{CH}_3}{\text{CH}}-\text{C}_2\text{H}_5$	Optically active laevorotatory compound			69	112
C_5	$-\text{C}_5\text{H}_{11}$	Isomer mixture enriched in the higher melting isomer		96-100		148
C_6	$-\text{C}_6\text{H}_{13}$	Isomer mixture enriched in the lower melting isomer		73-76		137
C_7	$-\text{C}_7\text{H}_{15}$	Isomer mixture		66		130.5
C_8	$-\text{C}_8\text{H}_{17}$	Isomer mixture	60.5	119.5		125.5
C_{10}	$-\text{C}_{10}\text{H}_{21}$	Isomer mixture	74			125.5
C_{12}	$-\text{C}_{12}\text{H}_{25}$	Isomer mixture	72			125

Columns

The stationary phases were deposited on Chromosorbs (particle size 0.15-0.20 mm) from methylene chloride solutions. For small amounts (1.1-1.6%) of the stationary phase C_7 on the support three Chromosorbs were used, W NAW, W AW and W AW DMCS, whereas for larger quantities and the remaining phases only Chromosorb W AW DMCS was used. The actual quantity of the liquid crystal on the support was calculated from the loss of weight when the liquid crystal was removed from the support by heating at 600°C . The packings were used in glass columns (2.1 m and 5 m \times 4 mm I.D.). The characteristics of the columns are given in Table II.

Chromatographic procedure

The measurements were made using a Pye Unicam GCV chromatograph adapted for physicochemical measurements by connecting the mercury manometer to the injector. A flame-ionization detector (FID) was used. The temperature of the

TABLE II
COLUMNS INVESTIGATED

Column No.	Stationary phase	Amount of stationary phase on support (%)	Chromosorb support	Weight of column packing (g)	Length of column (m)
1	C ₇	1.1	W AW	8.10	2.1
2	C ₇	1.6	W NAW	7.30	2.1
3	C ₇	1.2	W AW DMCS	7.38	2.1
4	C ₇	2.4	W AW DMCS	7.86	2.1
5	C ₇	4.1	W AW DMCS	7.57	2.1
6	C ₇	6.5	W AW DMCS	7.80	2.1
7	C ₇	8.2	W AW DMCS	7.76	2.1
8	C ₇	10.0	W AW DMCS	7.73	2.1
9	C _{5a}	5.4	W AW DMCS	7.80	2.1
10	C ₅	5.7	W AW DMCS	7.76	2.1
11	C ₆	2.0	W AW DMCS	7.52	2.1
12	C ₈	6.0	W AW DMCS	7.85	2.1
13	C ₁₀	5.4	W AW DMCS	7.79	2.1
14	C ₁₂	6.1	W AW DMCS	7.82	2.1
15	C ₇	5.0	W AW DMCS	18.95	5.0

injector was 180°C and that of the detector 160°C. Argon was used as the carrier gas. Before starting the measurements each column was heated for 2 h at a temperature 20°C higher than its temperature of transition from mesophase to isotropic liquid. To determine the retention characteristics, solutions of xylene isomers diluted 50-fold with cyclohexane were introduced by means of a 10⁻³-cm³ Hamilton microsyringe. The volumes of the samples were 2 · 10⁻⁵ cm³. The column temperature was usually varied in steps of 5°C and in steps of 1°C in the phase transition regions. The columns were heated at each temperature for 10–20 min to establish thermal equilibrium.

Measurements in the column heating stage were started after its cooling to room temperature, whereas in the column cooling stage they were started at a temperature higher than that of the clearing point. For each temperature the flow-rate of the carrier gas was set at 25 cm³/min, the pressure of the gas being read at the column inlet.

The column packings were characterized as follows:

- (1) The specific retention volume, V_g^N , given by the well-known formula⁷.
- (2) The retention volume per gram of column filling, $V_s = V_g^N \cdot \tau$, where τ is the percentage of the stationary phase on the support.
- (3) The separation ratio, $k = (t_R - t_m)/t_m$, where t_R is the retention time for the tested substance and t_m is the methane retention time.
- (4) Activity coefficients of the xylene isomers in the stationary phase at infinite dilution, $f^\infty = 273.2 R/V_g^N M p$, where R is the gas constant, M is the molecular weight of the stationary phase and p is the vapour pressure of the solute calculated from the Antoine equation.
- (5) The variations of the dissolution excess functions, calculated by using the activity coefficient values:

$$\Delta G^E = 2.3 RT \log f^\infty$$

$$\Delta H^E = 2.3 R \frac{d(\log f^\infty)}{d(1/T)}$$

$$\Delta S^E = (\Delta H^E - \Delta G^E)/T$$

The differentiation was performed by the graphical method.

(6) The dissolution (sorption) enthalpy of xylene isomers in the liquid crystal, calculated by using the dependence of the logarithm of the specific retention volume on the reciprocal of temperature $\log V_g^N = f(1000/T)$:

$$\Delta H = 19.17 \frac{\log V_g^N(T_1) - \log V_g^N(T_2)}{1/T_1 - 1/T_2} \text{ J/mole}$$

Standard thermodynamic properties are employed, in accordance with Kelker's considerations⁷.

(7) The differences between the enthalpies and entropies of the *p*- and *m*-xylene isomers

$$-\Delta H_p^0 + \Delta H_m^0 = 2.3 AR$$

$$\Delta S_p^0 - \Delta S_m^0 = 2.3 BR$$

where *A* and *B* are coefficients in the equation

$$\log \frac{t_{R(p)} - t_m}{t_{R(m)} - t_m} = A \frac{1}{T} + B$$

use being made of the relationships

$$\log \frac{V_{g(p)}^N}{V_{g(m)}^N} = \frac{-\Delta H_p^0 + \Delta H_m^0}{2.3 RT} + \frac{\Delta S_p^0 - \Delta S_m^0}{2.3 RT}$$

$$\log \frac{V_{g(p)}^N}{V_{g(m)}^N} = \log \frac{t_{R(p)} - t_m}{t_{R(m)} - t_m}$$

where $V_{g(p)}^N$, $V_{g(m)}^N$ are the specific retention volumes, ΔH_p^0 , ΔH_m^0 are the dissolution enthalpies and ΔS_p^0 , ΔS_m^0 are the dissolution entropies of *p*- and *m*-xylene, respectively, and $t_{R(p)}$, $t_{R(m)}$, t_m are the retention times for *p*- and *m*-xylene, and methane, respectively.

(8) Electron microphotographs made using a JEOL Type JEM-6A transmission electron microscope by the one-step carbone-platinum shaded-replica method. A similar method was employed for testing the surfaces of the supports⁸.

(9) The selectivity of columns with a liquid crystalline stationary phase, which is characterized by the relative retention time and resolution. The relative retention time is given by:

$$r_{1,2} = \frac{t_{R(p)} - t_m}{t_{R(m)} - t_m}$$

The column resolution was determined as $R = (t_{R(p)} - t_{R(m)}) / u/2w_p$ where *u* is the speed of the recorder tape and w_p is the *p*-xylene peak width at half-

height. This relationship was used since it was not possible to determine the resolution over the whole temperature range from a single chromatogram. Only the peak width of *p*-xylene was measured, since it was found that the peak width for *m*-xylene is the same within experimental error.

(10) Column efficiencies, in terms of HETP using *p*-dichlorobenzene in benzene solution as the test substance.

RESULTS AND DISCUSSION

Most tests were performed using the C_7 phase. The quantity of this phase on the support was adjusted so as to allow the detection of differences in the liquid crystal-support interactions. Such differences are usually most evident when the quantities of the phase on the support are small and they depend on the kind of support used. Therefore at small coverages three supports were used. At higher coverage, Chromosorb W AW DMCS was used which seems to have the best analytical properties of the three Chromosorbs tested. We did not observe any significant differences in the behaviour of the liquid crystal-support system for the three supports at coverages of 1.1–1.6% C_7 phase. It was found, however, that the non-silanized supports react in similar manner with the liquid crystal, but differently from the silanized support. This confirms our earlier observations³.

The variation of the specific retention volume of xylene isomers with temperature in the solid state range, in the mesophase and in the isotropic liquid for the C_7 phase is shown in Fig. 1. This plot is typical of liquid-crystalline stationary phases^{9–11}. The phase transition region, ending with the transition of the solid to the mesophase, is related to the thickness of the liquid crystal layer on the surface of the support. Owing to their different interactions with the support and with each other, the molecules in the liquid crystal layer are in various energy states, and therefore they require different additional energies to undergo phase transitions; thus melting proceeds not at one temperature but over a temperature range. The pre-transition effects in the liquid crystals, consisting in the changes of the liquid crystal structure prior to the phase transition, also play a significant role. In addition, the fact that the investigated phases are isomer mixtures has an effect on the range of the phase transition temperature. Fig. 1 shows the shifts of the chromatographically determined phase transition temperatures with respect to those obtained by the thermo-optical method.

In the mesophase range the value of V_g^N decreases linearly with increasing temperature, as for the isotropic phases. Above a certain temperature the values of the specific retention volume are somewhat higher than would be expected from the linear relationship of $\log V_g^N = f(1000/T)$. The deviation of this function from linearity is related, among other things, to the lowering of the ordering of the mesophase molecules S . This is supported by the similarity of plots of $\log V_g^N = f(t)$ and $S = f(t)$ (ref. 12), which both exhibit a change in slope. Lower ordering of the stationary phase is accompanied by better dissolution of the solute.

In Fig. 2 are presented the variations of the retention volume with temperature for the C_8 , C_{10} and C_{12} phases deposited in similar amounts on the support. Phases C_{10} and C_{12} are smectics over the whole mesophase range. Hence, the transition from the mesophase to the isotropic liquid is more distinct than that from the nematic state

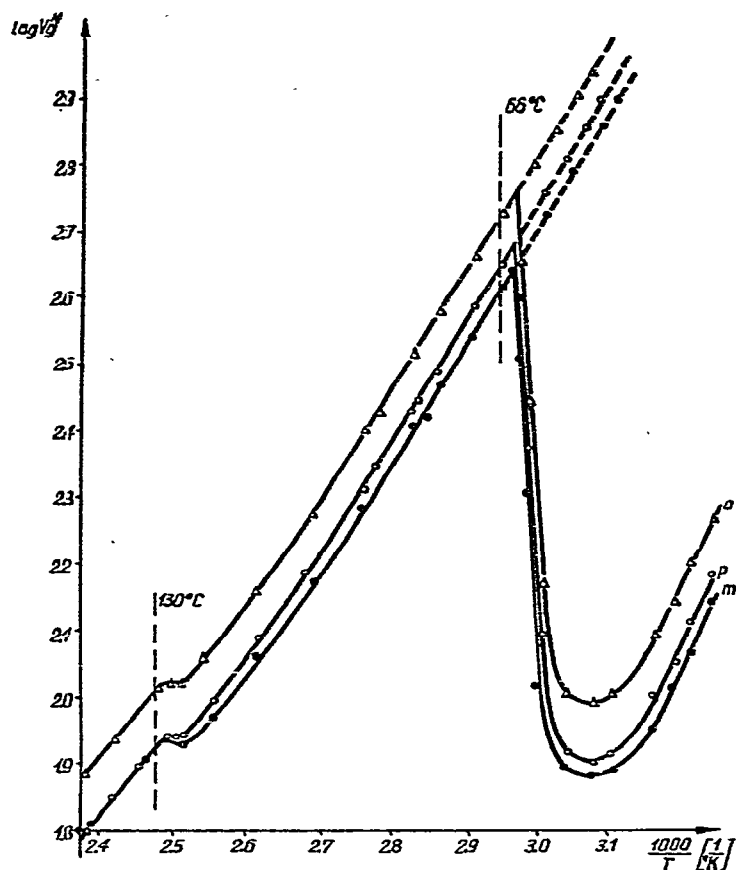


Fig. 1. Variation of the retention volume with column temperature for *o*-, *m*- and *p*-xylene isomers on column 6 (Table II). The dashed line represents the results for the supercooled phase.

to the isotropic liquid, phase C_8 . For the latter phase we observe a phase transition connected with the change of structure from the smectic to the nematic. The change in the retention at the phase transition temperature is related to the change of the mechanism of interaction of the tested substance with the stationary phase.

In Fig. 3 the variation of the retention volume with column temperature is compared for the C_5 and C_{5a} phases. The latter does not undergo supercooling and the same relationship is obtained for it during repeated cycles of heating and cooling of the column. For C_5 different plots are obtained depending on the measurement conditions. If the column is heated a long time after its conditioning, we obtain the plot represented by the solid line. In the cooling stage, supercooling of the column takes place according to line 2. Heating of the column within 12 h of cooling results in a plot that first coincides with line 1 and then proceeds in accordance with the solid line at higher temperatures, and upon subsequent column cooling follows line 2.

Some liquid crystals can remain in the supercooled state for a couple of months¹³. It is therefore probable that the observed behaviour is related to the strong tendency to supercool, with the possibility of crystallization in certain regions. A

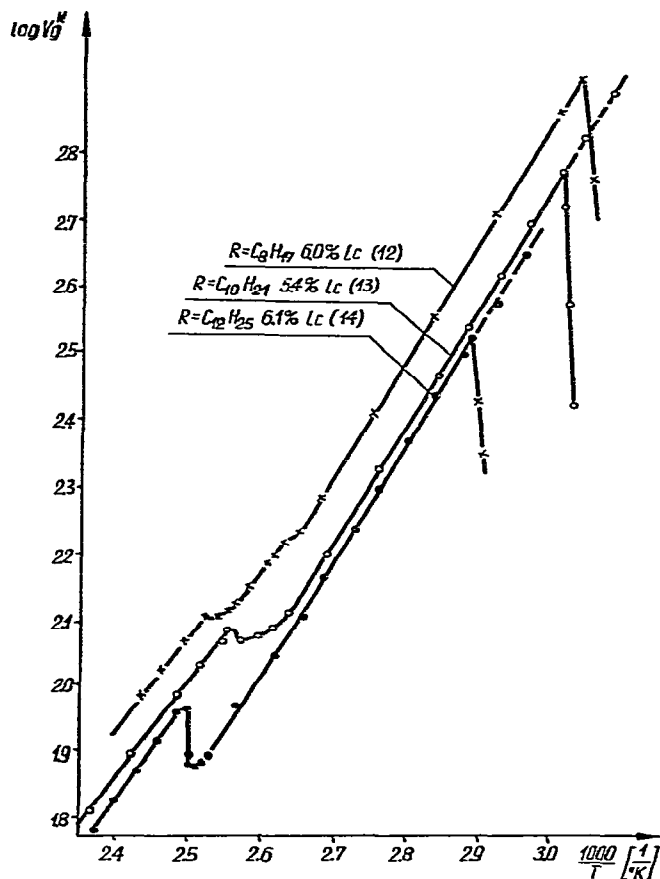


Fig. 2. Variation of the *p*-xylene retention volume with temperature for columns 12-14.

stable supercooled state was obtained for the C_5 phase even at a temperature 60°C lower than the melting point. The maxima in Fig. 3 correspond to the melting points of the pure isomers.

Distinct differences were observed in the course of the function $\log k = f(1000/T)$ for packings with small amounts of the stationary phase on the support in the solid state range (Fig. 4). When Chromosorb W NAW was used as the support, the values of the separation ratio were much lower than those for Chromosorb W AW DMCS. In Fig. 5 the temperature dependence of the separation ratio is given for columns with different stationary phase contents on the support. All plots are similar; only in the case of columns with 1.2 and 2.4% stationary phase contents were the phase transitions less pronounced and at lower temperatures. In the solid state temperature range the separation ratios for columns with a stationary phase content of 4% exhibited very similar minimum values at about 52°C . The dead volume is approximately the same for all columns and the retention volumes are very similar. The amount of stationary phase on the support is not essential in this case, and only the surface area of the support and stationary phase in contact with the gas is important.

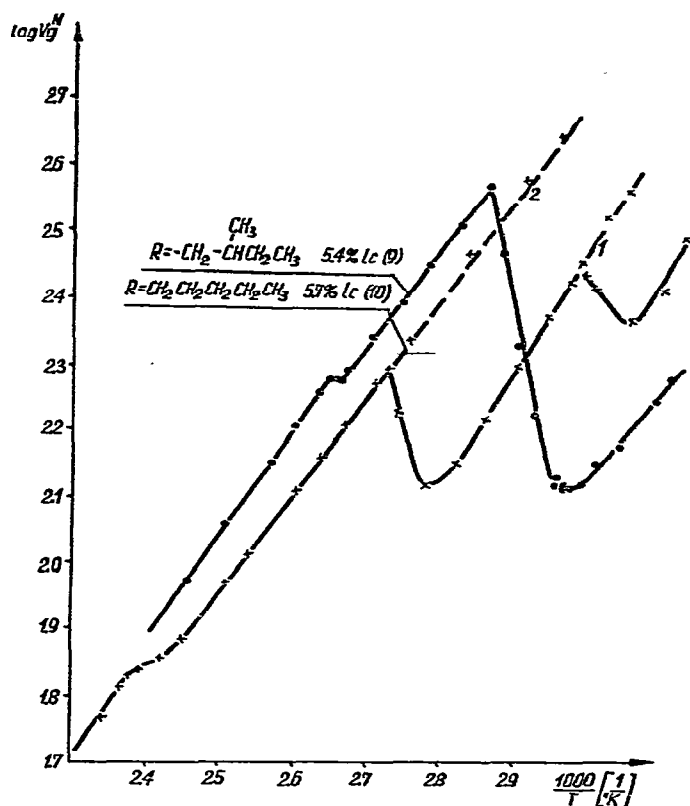


Fig. 3. Variation of the *p*-xylene specific retention volume with temperature for columns 9 and 10.

Thus in the solid state temperature range, adsorption takes place chiefly on the stationary phase. The situation is different when the content of the stationary phase on the support is lower than 4%. For such packings the retention volume in the solid state range (about 52°C) is lower than for columns with a higher stationary phase content. In this case the amount of stationary phase is probably too small to uniformly cover the support, and adsorption phenomena on the support occur. Moreover, with small quantities of the stationary phase, the support surface may react with all of the stationary phase. This results in an increase of the melting point of the stationary phase with its increasing content on the support (Fig. 5).

The observed increase of the separation ratio in the vicinity of the melting point is related to the partial melting of the stationary phase, and the significant differences in its value are related to the dissolution of the solute in the increasing volume of the stationary phase. In Fig. 5 a change of the clearing temperature can also be seen, which, like the melting point, increases with increasing content of the stationary phase on the support.

Fig. 6 presents the variation of the retention volume per gram of column packing with the content of the stationary phase on the support. At 72°C, *i.e.*, within the mesophase range, V_S is a linear function of the amount of the stationary phase

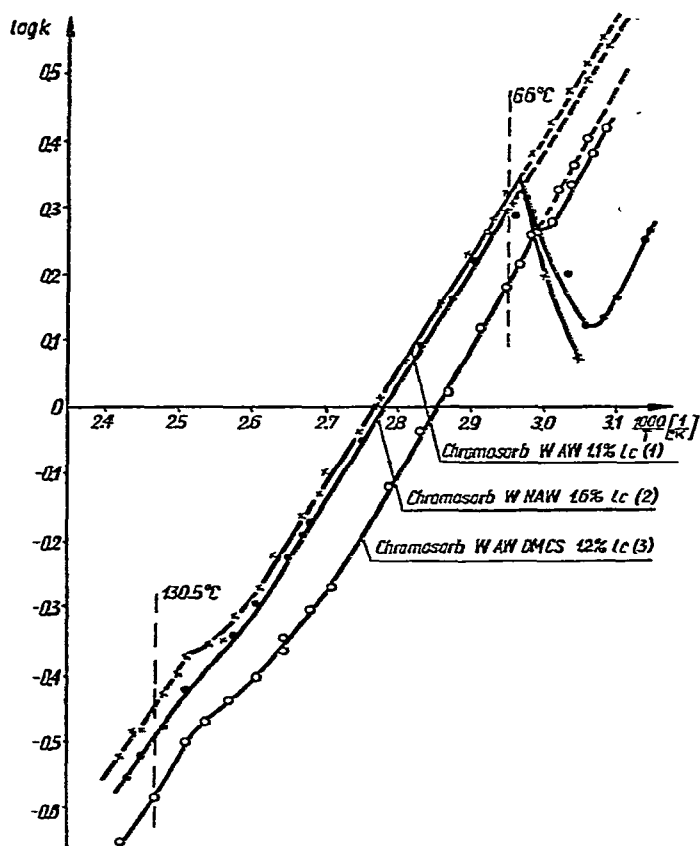


Fig. 4. Variation of the separation ratio with temperature for columns 1, 2 and 3 with the heptyl phase (C_7) on Chromosorb W AW, W NAW and W AW DMCS. Test substance: *p*-xylene.

within the range investigated. In the solid state temperature range, the support ceases to affect the retention volume at stationary phase contents of about 5%. This is related to the thickness of the liquid-crystalline stationary phase layer influenced by the support surface. This thickness is dependent on the kind of support and liquid-crystalline stationary phase, and can vary from 2 nm¹⁴ to 100 nm¹⁵.

Table III gives the enthalpies of *p*-xylene dissolution in the C_7 phase deposited in different amounts on Chromosorb W AW DMCS. Only the temperature ranges in which the relationship $\log V_g^N = f(1000/T)$ was linear were considered. Two ranges, 66–84°C and 104–124°C, correspond to the mesophase, whereas the third, 131–145°C, corresponds to the isotropic liquid. The dissolution enthalpies obtained for the 1.2% stationary phase content differ significantly from those obtained for other contents. In the second range, corresponding to the pre-transition range, the results are subject to an error resulting from that the fact that the dependence of the retention volume on temperature is not completely linear. The differences in the dissolution enthalpies between the first and third temperature ranges of about 7.5 kJ/mole indicates the stronger interaction of *p*-xylene molecules with the mesophase as compared with the

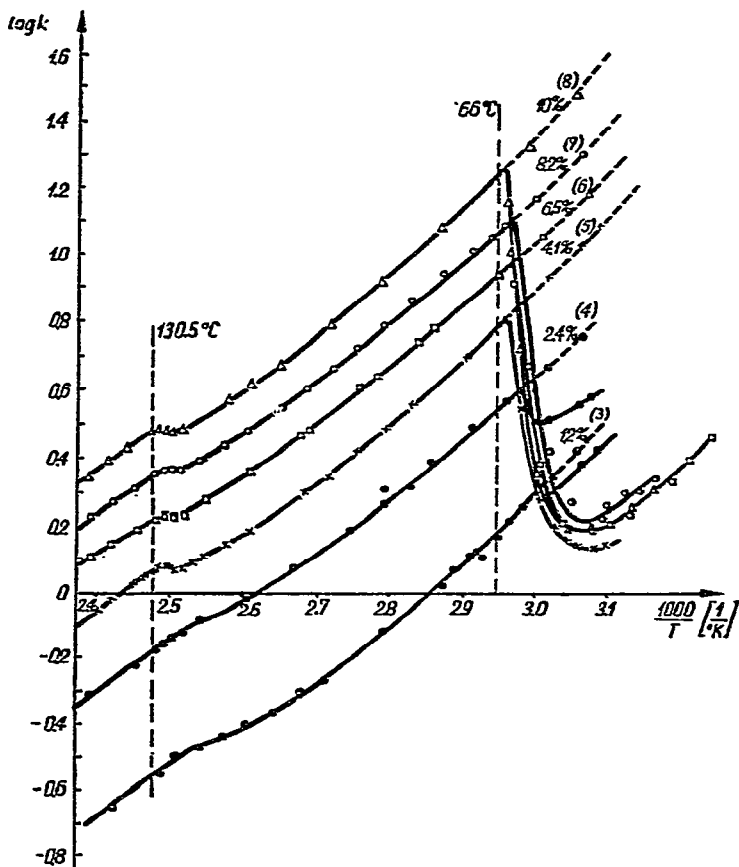


Fig. 5. Variation of the separation ratio with temperature for columns 3–8 with various amounts of the heptyl phase (C_7) on Chromosorb W AW DMCS. Test substance: *p*-xylene.

isotropic phase. A similar conclusion can be made from Table IV which gives the enthalpies of dissolution in the mesophase, $\Delta H(A)$, and in the isotropic liquid, $\Delta H(I)$, as well as the enthalpy differences $\Delta H(A) - \Delta H(I)$ and the entropy differences $\Delta S(A) - \Delta S(I)$ for several stationary phases.

Table V summarizes the dissolution enthalpy and entropy differences for *p*- and *m*-xylenes in the mesophase for different stationary phases. The dissolution enthalpy and entropy in the mesophase are lower for *p*-xylene, which demonstrates its stronger solvent–solute interaction and higher solution ordering as compared with *m*-xylene. As the *p*-xylene molecules pass from the disordered vapour to the ordered solution they can react strongly with the mesophase owing to the advantageous geometry, and a significant decrease in translation and rotation takes place. The resulting loss of entropy is balanced by the enthalpy difference and *p*-xylene has a greater solubility than *m*-xylene.

For two cases, *i.e.*, the heptyl phase (C_7) deposited 1.6% on Chromosorb W NAW and 6.5% on Chromosorb W AW DMCS, the sorption enthalpy of *p*-xylene was calculated in the solid state temperature range. The results obtained are 45 kJ/

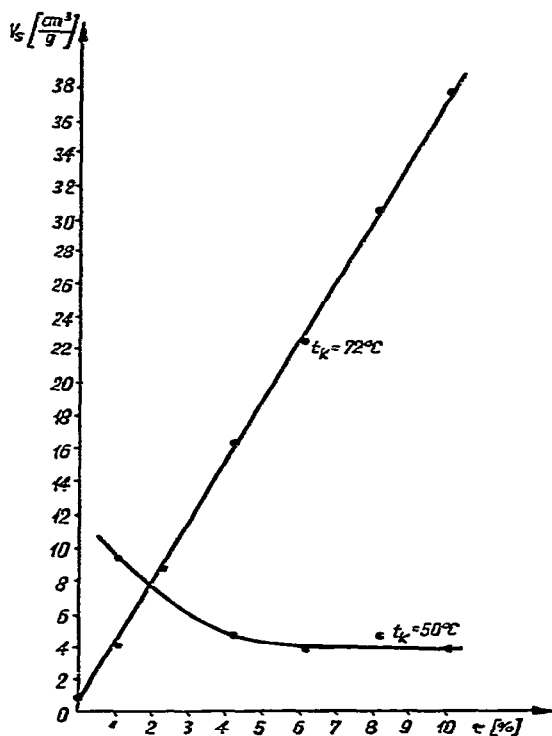


Fig. 6. Variation of *p*-xylene retention volume per unit support weight with percentage of the heptyl phase (C) deposited on Chromosorb W AW DMCS.

TABLE III

ENTHALPIES (kJ/mole) OF *p*-XYLENE DISSOLUTION IN THE HEPTYL PHASE DEPOSITED ON CHROMOSORB W AW DMCS

Quantity of the phase (%)	Temperature range (°C)		
	66-84	104-124	131-145
1.2	-37.6		-30.6
2.4	-35.3	-28.2	-28.7
4.1	-36.4	-27.5	-28.7
6.5	-36.0	-27.2	-28.4
8.2	-36.0	-26.8	-28.3
10.0	-35.9	-28.0	-29.0

mole and 41 kJ/mole respectively for the two packings. The difference between the two values can be explained in terms of the contribution of the uncoated support to the process of sorption, which is greater in the case of the packing with the smaller stationary phase content and the non-silanized Chromosorb.

In Fig. 7 is presented the variation of the activity coefficient of xylene isomers in the liquid-crystalline stationary phase. The activity coefficient of *m*-xylene has the highest value in the range of temperatures studied. The values of the activity coefficients

TABLE IV
 ENTHALPIES AND ENTHALPY AND ENTROPY DIFFERENCES OF *p*-XYLENE DISSOLUTION IN THE MESOPHASE AND IN THE ISOTROPIC LIQUID OF VARIOUS STATIONARY PHASES

Stationary phase	Amount of stationary phase on support (%)	Temperature range (°C)		$\Delta H(A)$ (kJ/mole)	$\Delta H(I)$ (kJ/mole)	$\Delta H(A) - \Delta H(I)$ (kJ/mole)	$\Delta S(A) - \Delta S(I)$ (J/°K·mole)
		Mesophase	Isotropic liquid				
C ₆	2.0	72-108		-34.4			
C ₇	6.5	66-84	131-145	-36.0	-28.4	-7.6	-25.2
C ₈	6.0	56-104	123-138	-35.5	-27.9	-7.6	-18.6
C ₁₀	5.4	60-105	119-150	-35.9	-28.2	-7.7	-19.7
C ₁₂	6.1	76-104	128-148	-36.0	-29.4	-6.6	-16.5

TABLE V
ENTHALPY AND ENTROPY DIFFERENCES OF *p*- AND *m*-XYLENE DISSOLUTION

Stationary phase	Amount of stationary phase on support (%)	Mesophase temperature range (°C)	$\Delta S_p - \Delta S_m$ (J/°K·mole)	$\Delta H_p - \Delta H_m$ (kJ/mole)
C ₆	2.0	72–108	–1.9	–0.8
C ₇	6.5	66–84	–1.3	–0.6
C ₈	6.0	56–104	–0.8	–0.4
C ₁₀	5.4	60–105	–0.6	–0.3
C ₁₂	6.4	76–104	–1.2	–0.6

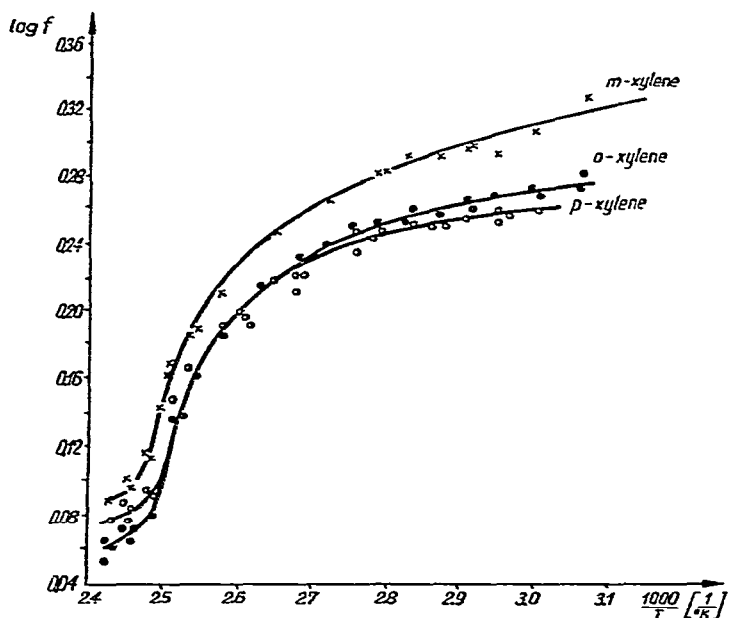


Fig. 7. Temperature variation of the activity coefficients of xylene isomers in 65% heptyl phase (C₇) deposited on Chromosorb W AW DMCS (column 6).

of *o*- and *p*-xylenes vary with the phase condition of the liquid crystal. The activity coefficients of *o*-xylene, higher in the mesophase than those for *p*-xylene, change their sequence in the isotropic liquid. Similar relationships have been observed previously¹⁶.

Fig. 8 shows the thermodynamic excess functions of *p*-xylene dissolution in the stationary phase as a function of reciprocal temperature. The excess thermodynamic potential has the highest value in the mesophase range since interaction between the liquid crystal and *p*-xylene molecules is greatest in that phase. This is in accord with the mechanism discussed by Martire *et al.*¹⁷. At the clearing point and in the pre-transition range, the interactions and the excess thermodynamic potential decrease and the dissolution excess enthalpy and entropy assume extreme values.

The differences in the properties of the liquid crystal–support systems for silanized and non-silanized supports are reflected in the results of microscopic

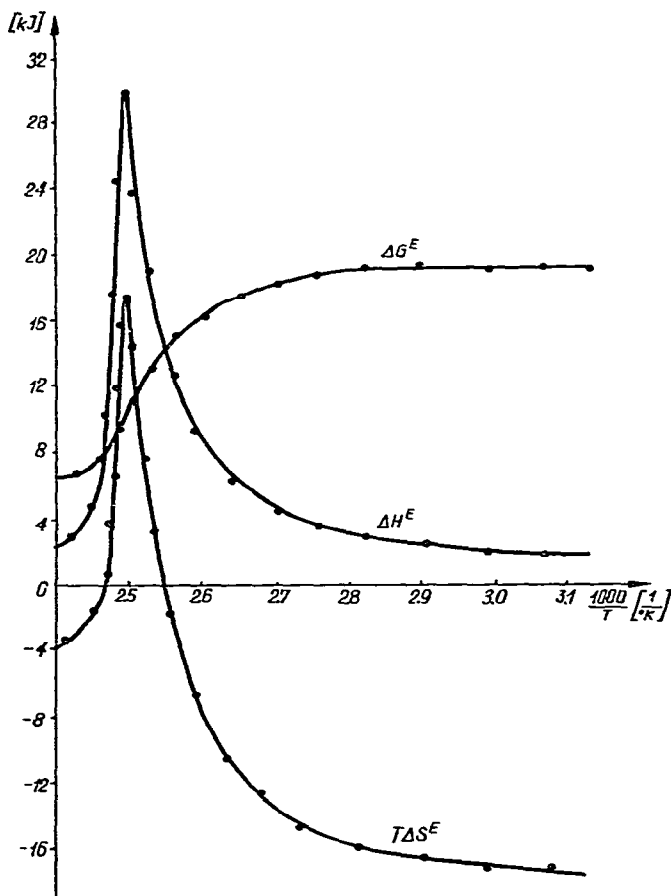


Fig. 8. Temperature variation of the excess temperature functions of *p*-xylene in a liquid crystal solution on column 6.

investigations. Fig. 9 shows the surface of Chromosorb W AW DMCS, and Fig. 10 the surface of the same Chromosorb onto which 1.2% of the C_7 stationary phase have been deposited. Fig. 10 clearly reveals patterns which are not seen on the Chromosorb surface without the stationary phase. These patterns probably correspond to agglomerations of the stationary phase. No such agglomerations have been observed on Chromosorb W NAW or W AW on which 1.6 and 1.1% of the C_7 phase were deposited. This indicates that on non-silanized supports the liquid-crystalline phase is distributed more uniformly and therefore is under greater influence from the support than in the case of silanized Chromosorb. The lower wettability of the silanized Chromosorb as compared with the non-silanized products may also contribute to this effect.

In Fig. 11 is presented the variation of the relative retention times of xylene isomers with the reciprocal temperature [$r_{1,2} = f(1000/T)$] for packings with 1.2 and 10% of the heptyl phase (C_7) on the support. It was found that for a packing with a small quantity of the stationary phase on the support (1.2%) the nature of this

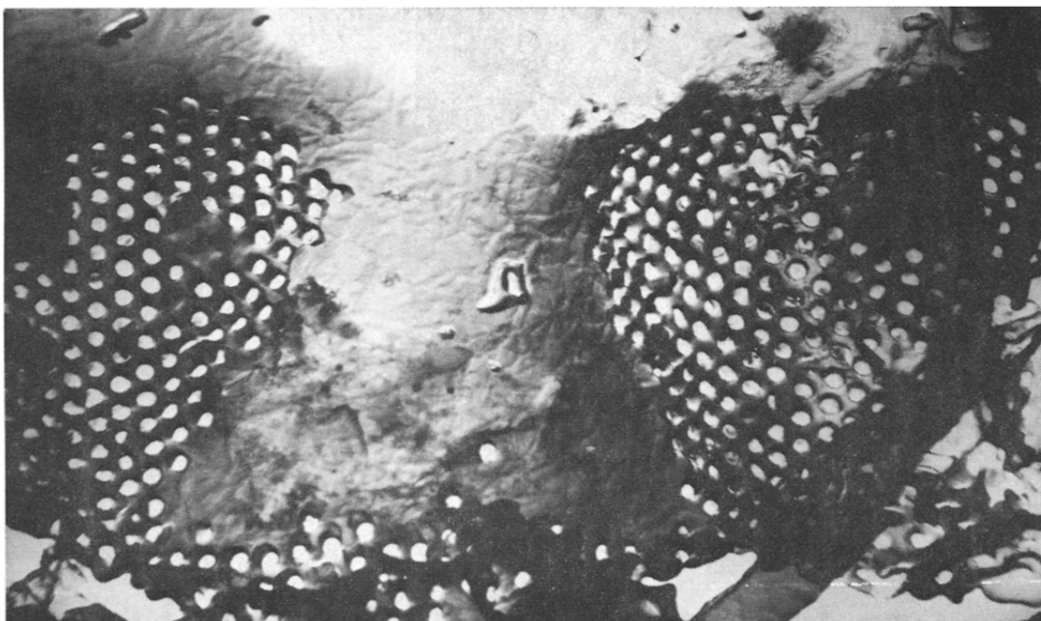


Fig. 9. Surface of the Chromosorb W AW DMCS support. Magnification $\times 11,160$.

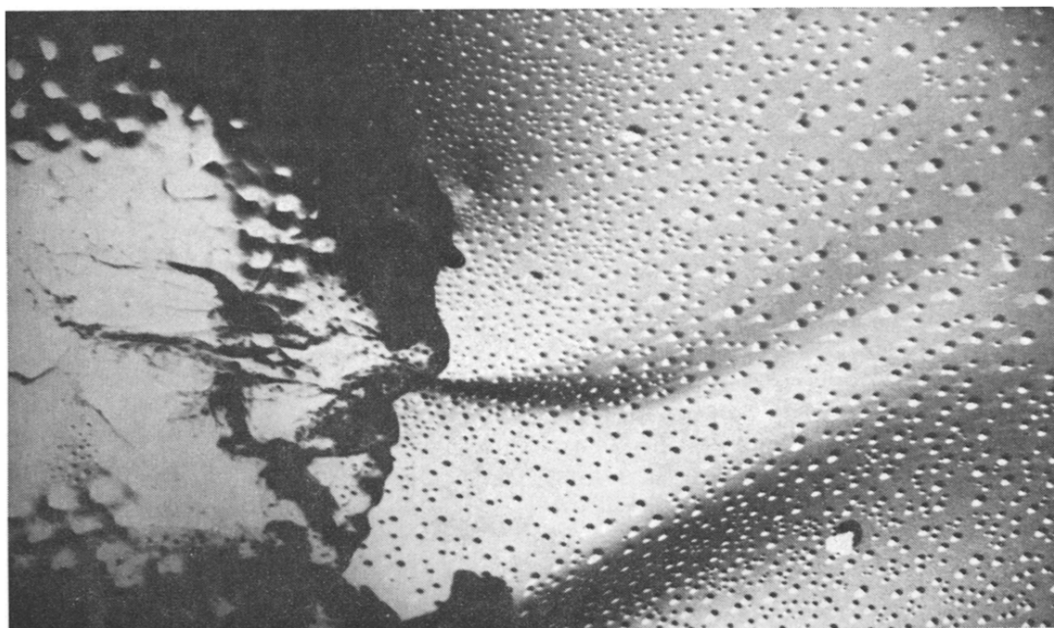


Fig. 10. Surface of the Chromosorb W AW DMCS support upon which 1.2% C₇ stationary phase has been deposited. Magnification $\times 10,440$.

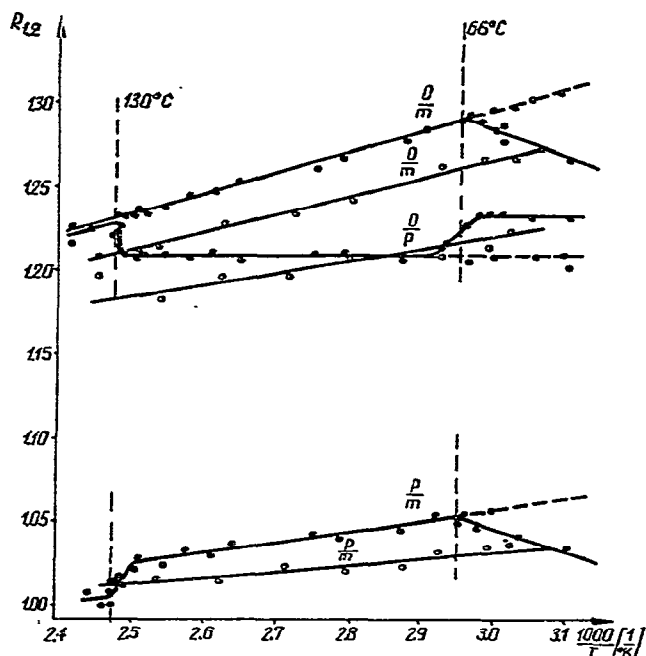


Fig. 11. Temperature dependence of the relative retention times of xylene isomers on column 8 (●) and column 3 (○).

relationship is different and the values of $r_{1,2}$ are lower than for packings with a higher stationary phase content. For packings with stationary phase contents greater than 4%, the values of the relative retention times are independent of the amount of stationary phase.

The plots of relative retention times *versus* reciprocal temperature are typical for azoxy-compounds. Similar plots were observed for other cyanoazoxybenzene alkyl carbonates and analogues^{4,5}. The relative retention times of *p*- and *m*-xylenes and *o*- and *m*-xylenes attain a maximum at the melting point and then decrease linearly with reciprocal temperature. In the vicinity of the clearing point the relative retention time for *p*- and *m*-xylenes decreases rapidly, reaching values close to unity. The relative retention time for *o*- and *m*-xylenes, in most cases in the mesophase range, is only slightly dependent on temperature.

Similar variations of relative retention time with the column temperature were obtained for the remaining smectic and nematic liquid crystals. However, a different plot was obtained for the C_{5a} phase (Fig. 12) which is due to the cholesteric structure of the mesophase. The plots do not show the characteristic points corresponding to the transition from the mesophase to the isotropic liquid. In the case of smectic liquid crystals (the octyl, decyl and dodecyl phases) the relative retention time of *p*- and *m*-xylenes is less strongly dependent on temperature than in the case of the nematic liquid crystals (the pentyl and heptyl phases).

Table VI summarizes the maxima of the relative retention times, which differ only slightly. When the stationary phases are supercooled to 50°C there is a strong dependence of the relative retention times on the extent of supercooling. The higher

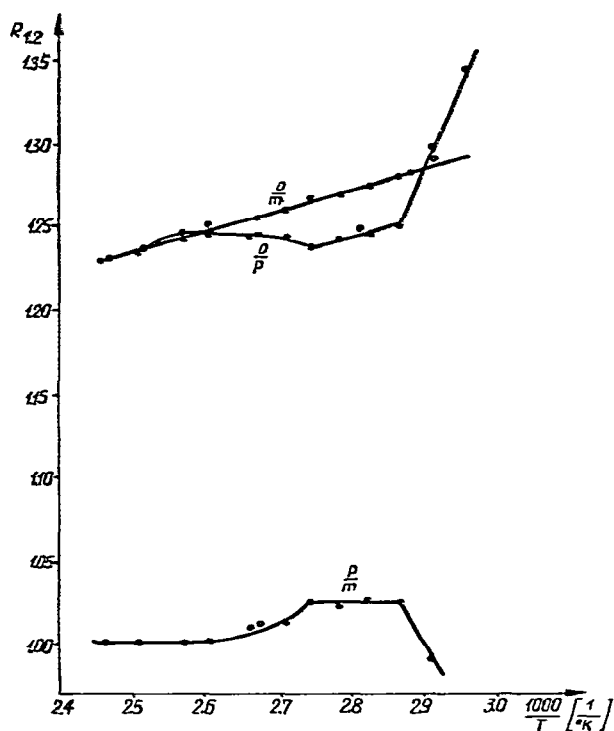


Fig. 12. Temperature dependence of relative retention times of xylene isomers in 5.4% phase C_{5a} deposited on Chromosorb W AW DMCS in column 9.

TABLE VI

MAXIMUM RELATIVE RETENTION TIMES FOR *p*- AND *m*-XYLENE

Stationary phase	Temperature of column ($^{\circ}C$)	$r_{p,m(max.)}$	$r_{p,m(max.)}$ at $50^{\circ}C$ (supercooling)
C_5	86	1.050	1.064
C_7	68	1.053	1.058
C_8	54	1.046	1.049
C_{10}	60	1.039	1.042
C_{12}	74	1.049	1.055

the melting point of the stationary phase the higher is the relative retention time for *p*- and *m*-xylene at $50^{\circ}C$. This relationship holds precisely for stationary phases with mesophases of similar stability (C_5 and C_7 phases). The similarity of the mesophase stabilities can be seen in the same value of the slope of the $r_{1,2} = f(1000/T)$ curve.

The efficiencies of the tested columns revealed similar dependences of the HETP on the carrier gas flow-rate. The optimum carrier gas flow-rates lie within the range 25–40 cm^3/min and the minimum HETP values varied from 0.5 to 0.8 mm.

For the investigated quantities of the stationary phases on Chromosorb W AW DMCS, small differences occur in the slope of the right branch of the curve, thus the

diffusion conditions in the stationary phase are very similar irrespective of its amount on the support. Hence, we can conclude that an increase of the quantity of the stationary phase on the support does not produce an increase of the layer thickness, but of the coverage of the free support surface. This is confirmed by the microscopic investigations.

For phase C_7 , HETP was found to depend weakly on temperature in the mesophase range (Fig. 13). In the solid state temperature range the efficiency of the column is small, but increases rapidly and is approximately constant in the mesophase, isotropic liquid and supercooled liquid. A similar dependence was found earlier for small-bore packed micro-columns⁶.

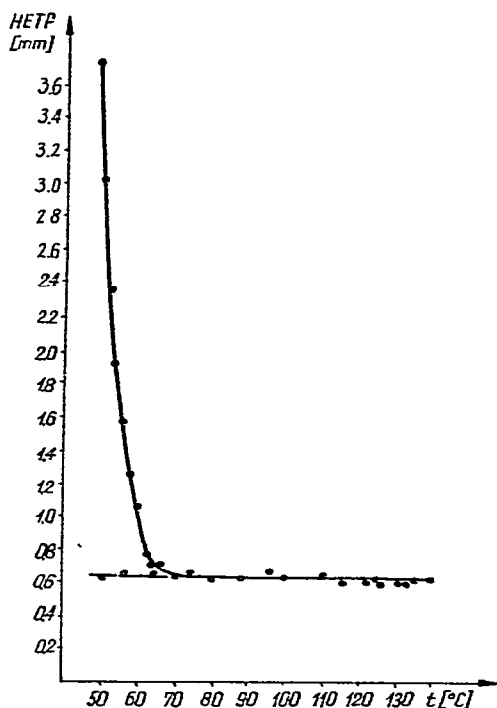


Fig. 13. Temperature dependence of HETP for 6.5% phase C_7 , deposited on Chromosorb W AW DMCS in column 6.

In Figs. 14 and 15 the column resolution is given for *p*- and *m*-xylene isomers as a function of temperature. Fig. 14 shows that the nature of the plot changes when passing from columns with a low stationary phase (C_7) content to columns with a higher content. For the column containing 4.1% C_7 phase the resolution is maximal. Similar relationships and similar maximum values were obtained for the remaining stationary phases. In Fig. 15 an example is given of the resolution for the pentyl phase, account also being taken of its supercooling.

Attempts to separate disubstituted benzene isomers have shown that, except for phase C_{5a} , these phases are suitable for this purpose. Phase C_{5a} is cholesteric and

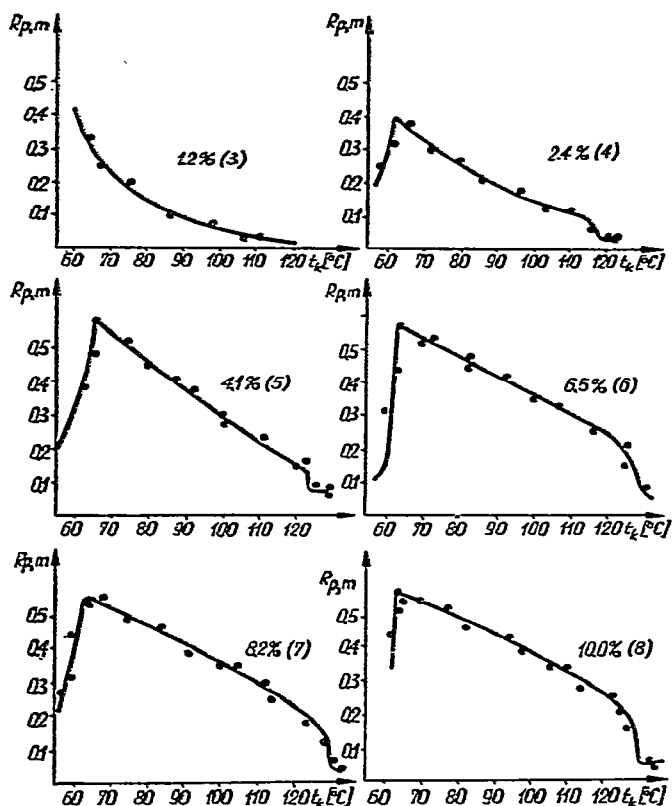


Fig. 14. Column resolution as a function of temperature for columns 3-8 of different contents of phase C₇ on Chromosorb W AW DMCS.

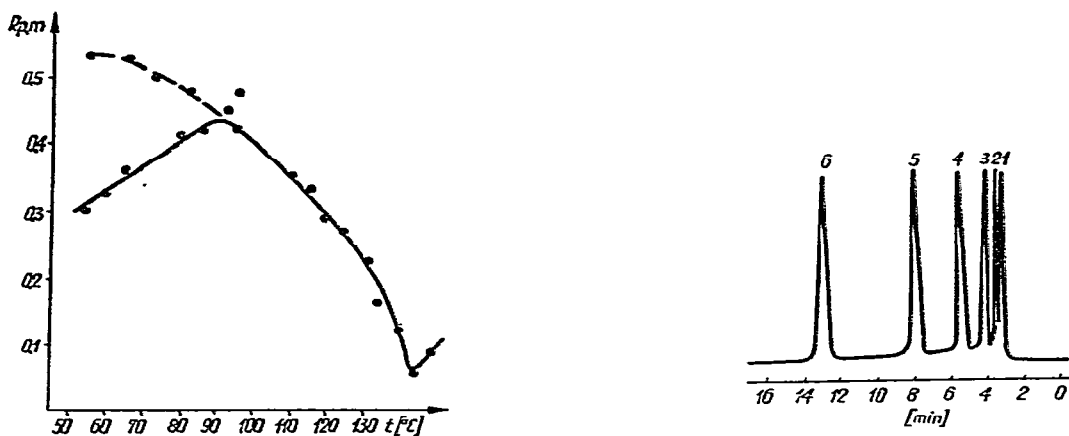


Fig. 15. Column resolution as a function of column temperature for 5.7% phase C₅ deposited on Chromosorb W AW DMCS.

Fig. 16. Separation of *n*-alkanes on column 15. Column temperature: 90°C. Argon flow-rate: 40 cm³/min. Peaks: 1 = pentane; 2 = hexane; 3 = heptane; 4 = octane; 5 = nonane; 6 = decane.

its different properties make it unsuitable for separating isomers of this kind. Better separations are obtained on nematic phases than on smectic ones. The best separations were obtained on the hexyl and heptyl phases on Chromosorb W AW DMCS. Isomers of xylene, chlorotoluene, bromotoluene, ethyltoluene and dichlorobenzene, as well as components of homologous series, were separated. Examples of the resolutions obtained are shown in Figs. 16 and 17. The selectivity of the most efficient *p*-cyanoazoxybenzene *p'*-alkyl carbonates for disubstituted benzene isomers is so high that, in normal analytical columns, resolutions similar to those on columns of smaller diameters are obtained.

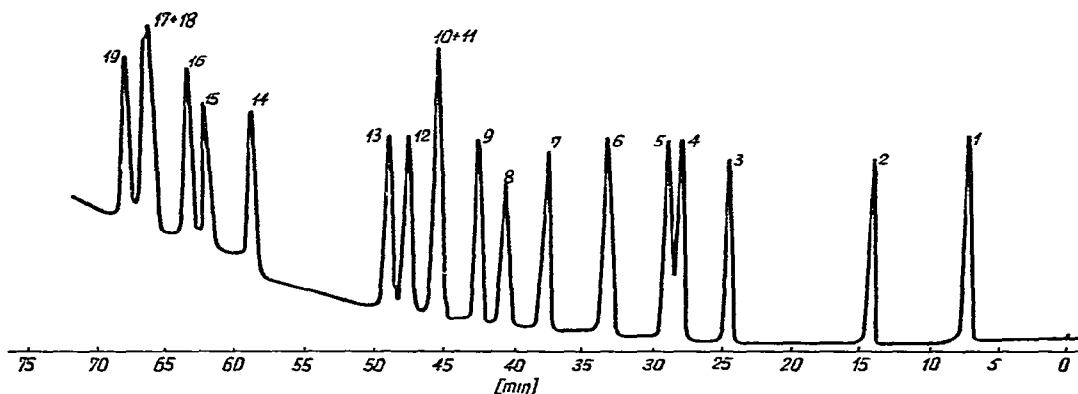


Fig. 17. Separation of a mixture on column 15. Argon flow-rate: 40 cm³/min. Initial temperature held at 55°C for 5 min then increased at a rate of 1°C/min to 120°C. Peaks: 1 = benzene; 2 = toluene; 3 = ethylbenzene; 4 = *m*-xylene; 5 = *p*-xylene; 6 = *o*-xylene; 7 = propylbenzene; 8 = *m*-ethyltoluene; 9 = *p*-ethyltoluene; 10 = *o*-ethyltoluene; 11 = *o*-chlorotoluene; 12 = *m*-chlorotoluene; 13 = *p*-chlorotoluene; 14 = *m*-dichlorobenzene; 15 = *p*-dichlorobenzene; 16 = *o*-bromotoluene; 17 = *o*-dichlorobenzene; 18 = *m*-bromotoluene; 19 = *p*-bromotoluene.

REFERENCES

- 1 Z. Witkiewicz, Z. Suprynowicz, J. Wójcik and R. Dąbrowski, *Pol. J. Chem.*, 52 (1978) 1495.
- 2 Z. Witkiewicz, Z. Suprynowicz, J. Wójcik and R. Dąbrowski, *J. Chromatogr.*, 152 (1978) 323.
- 3 S. Popiel and Z. Witkiewicz, *Biul. Wojsk. Akad. Tech.*, 27, No. 4 (1978) 29.
- 4 S. Popiel and Z. Witkiewicz, *Biul. Wojsk. Akad. Tech.*, 27, No. 4 (1978) 39.
- 5 Z. Witkiewicz and S. Popiel, *J. Chromatogr.*, 154 (1978) 60.
- 6 Z. Witkiewicz, Z. Suprynowicz and R. Dąbrowski, *J. Chromatogr.*, 175 (1979) 37.
- 7 H. Kelker, *Advan. Liquid Crystals*, 3 (1978) 237.
- 8 Z. Suprynowicz and E. Tracz, *Chem. Anal. (Warsaw)*, 21 (1976) 1089.
- 9 L. C. Chow and P. E. Martire, *J. Phys. Chem.*, 75 (1971) 2005.
- 10 G. M. Janini, G. M. Muschik and W. L. Zielinski, Jr., *Anal. Chem.*, 48 (1976) 809.
- 11 S. Wasik and S. Chesler, *J. Chromatogr.*, 122 (1976) 451.
- 12 A. Saupe, *Angew. Chem., Int. Ed. Engl.*, 7 (1968) 97.
- 13 M. Jawdosiuk and E. Czarnecka, *Wiad. Chem.*, 31 (1977) 329.
- 14 J. Rayss, Z. Witkiewicz, A. Waksmundzki and R. Dąbrowski, *J. Chromatogr.*, 188 (1980) 107.
- 15 L. C. Chow and D. E. Martire, *J. Phys. Chem.*, 73 (1969) 1127.
- 16 M. Kelker and A. Verhelst, *J. Chromatogr. Sci.*, 7 (1969) 79.
- 17 D. E. Martire, A. Nikolić and K. L. Vasanth, *J. Chromatogr.*, 178 (1979) 401.