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LIQUID CRYSTALLINE STATIONARY PHASES WITH A CYCLOHEXYL RING IN THE MOLECULE

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SUMMARY

The selectivities and polarities of five liquid crystalline stationary phases, derived from cyclohexane and differing as regards the terminal substituents, were determined. The efficiency of the columns in which these stationary phases were deposited was established. The selectivities of the stationary phases are related to the type of mesophase and are comparable to those of other liquid crystalline stationary phases; likewise the efficiencies of the columns with these phases are comparable but the polarity is low.

INTRODUCTION

Interest in liquid crystalline stationary phases is increasing because of their practical usefulness in the separation and analysis of components of many mixtures. Also, liquid crystals are very useful for testing and acquiring a better knowledge of the interactions that take place between stationary phases and supports. The effects of the particular types of mesophase structure and of the molecular structure of the liquid crystals as stationary phases can also be studied chromatographically. All these possibilities have already been described[1–7].

In this work we studied the chromatographic properties of liquid crystalline stationary phases derived from cyclohexane. This group of compounds was chosen because their properties when applied as stationary phases have not previously been studied in detail. These tests are necessary in order to establish whether the presence of the cyclohexyl ring may change the properties of these liquid crystals compared with their analogues that only have aromatic rings in the molecules.
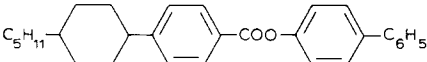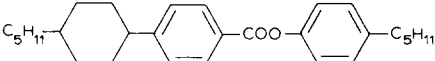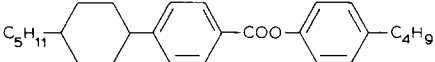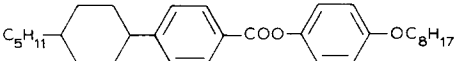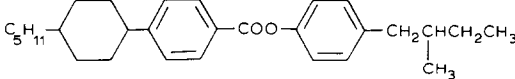
Liquid crystals with a cyclohexyl ring in the molecule have been used in the analysis of *cis* and *trans* isomers of 1,4-substituted cyclohexanes, methyl esters of higher fatty acids with one unsaturated bond and xylene isomers[8].

EXPERIMENTAL

Liquid crystalline stationary phases

The properties of compounds whose characteristics are given in Table I are

TABLE I

LIQUID CRYSTALS USED

Phase	Chemical formula	Phase transition temperatures (°C)*			
		In smectic		To nematic	To isotropic liquid
		B	A		
I	C_5H_{11}—⬡—⬡—COO—⬡—C_6H_5	(121.0)	(142.0)	154.5	267.0
II	C_5H_{11}—⬡—⬡—COO—⬡—C_5H_{11}	73.5	93.5	132.5	166.5
III	C_5H_{11}—⬡—⬡—COO—⬡—C_4H_9	72.5	90.0	120.5	158.0
IV	C_5H_{11}—⬡—⬡—COO—⬡—OC_8H_{17}	78.0	106.0	158.5	178.5
V	Mixture of II + III	67.0	92.0	127.5	163.0
		To smectic		To chole-steric	
VI	C_5H_{11}—⬡—⬡—COO—⬡—$CH_2CHCH_2CH_3$ $\overset{|}{CH_3}$		81.5	110.0	148.0

* In parentheses phase transition temperatures observed only during cooling are given.

tested. The production of these compounds has been described[9]. Their purity was checked by thin-layer chromatography and the phase transition temperatures were measured by the thermo-optical method with a polarizing microscope. The phase transition temperatures of compounds II, III, IV and VI were the same when the measurements were made during heating or cooling. The solid–smectic B–smectic A transitions observed on cooling compound I did not occur on heating.

Apart from single liquid crystals we tested the properties of a mixture containing 50% (w/w) of compounds II and III. This composition of the mixture was selected based on the phase plot obtained as a result of measurements of the melting and clearing temperatures and of the intermediate phase transition temperatures of melts with different proportions of the components. The phase plot obtained is shown in Fig. 1.

The single stationary phases and the mixed phase were deposited on Chromosorb W NAW of particle size 0.2–0.25 mm, previously conditioned for 2 h at 200°C. The stationary phases were deposited on the support in an amount of 15% from chloroform solutions by evaporation of the solvent in a vacuum evaporator. The packings prepared in this way were placed in 2.1 m × 4 mm I.D. glass columns. The columns were placed in the thermostat of a Pye Unicam GCV gas chromato-
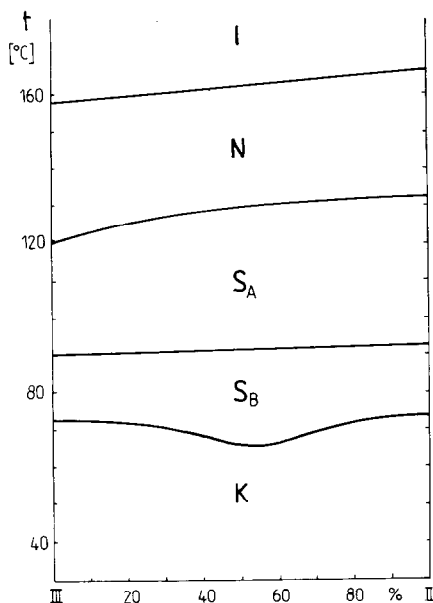
Fig. 1. Phase diagram for the mixture of the compounds II and III.

graph equipped with a flame-ionization detector. The temperature of the detector was 220°C and that of the injector was 260°C.

Selectivities of the stationary phases

The selectivities of the liquid crystalline stationary phases were determined from the dependences of the relative retention time and the retention indices of m- and p-diethylbenzene on temperature [ln $r_{p/m}$ = f($1000/T$) and I_x = f(t)]. Apart from diethylbenzene the mixture also contained n-octane, n-nonane, n-decane and n-dodecane. The retention times of these n-alkanes were used for calculating the dead time and the retention indices of the diethylbenzene isomers. A $1.5 \cdot 10^{-4}$ mm^3 portion of the mixture containing approximately equal amounts of the above components was injected into the column with a microsyringe. The retention times of the components were measured by means of a stop-watch.

The separation of diethylbenzene isomers was unsatisfactory for phases II, III and V in the temperature range 68–93°C (*i.e.*, for smectic B). Therefore, in this temperature range we used a mixture of the above-mentioned n-alkanes and only one diethylbenzene isomers. The retention indices were calculated from the generally known equation and the dead time utilized for this purpose and for calculating the relative retention times of p- and m-diethylbenzene was found from the n-alkane retention times[10].

Polarities of the stationary phases

The polarities of the stationary phases were characterized by the retention indices of standard substances according to the method of Rohrschneider[11] and McReynolds[12]. A mixture containing n-heptane, n-octane, n-nonane and n-decane

and, separately, the single test substances benzene, 1-butanol, 2-pentanone, 1-nitro-propane, pyridine and *m*- and *p*-xylene were fed into the column alternately. Xylene isomers were used additionally to measure the differences in the retention indices of compounds with different molecular shapes. The *n*-alkane mixture and the test substances were injected into the column in amounts of about 10^{-4} mm^3, and the retention times were measured with a stop-watch. The measurements were repeated several times. The column temperature was 120°C.

The retention indices were calculated by a statistical method described by Grobler and Balizs[13,14].

Column efficiencies

The efficiencies of columns containing the tested stationary phases were expressed in terms of effective plate numbers (n_{eff}) according to a method described by Kaiser[15]. The measurements were made at 145°C for phases I, II, III and V and at 159°C for phase IV. These temperatures correspond to the nematic phase of the liquid crystals. No measurements were made for phase VI as the lack of the nematic mesophase renders difficult its comparison with the remaining phases. The flow-rate of
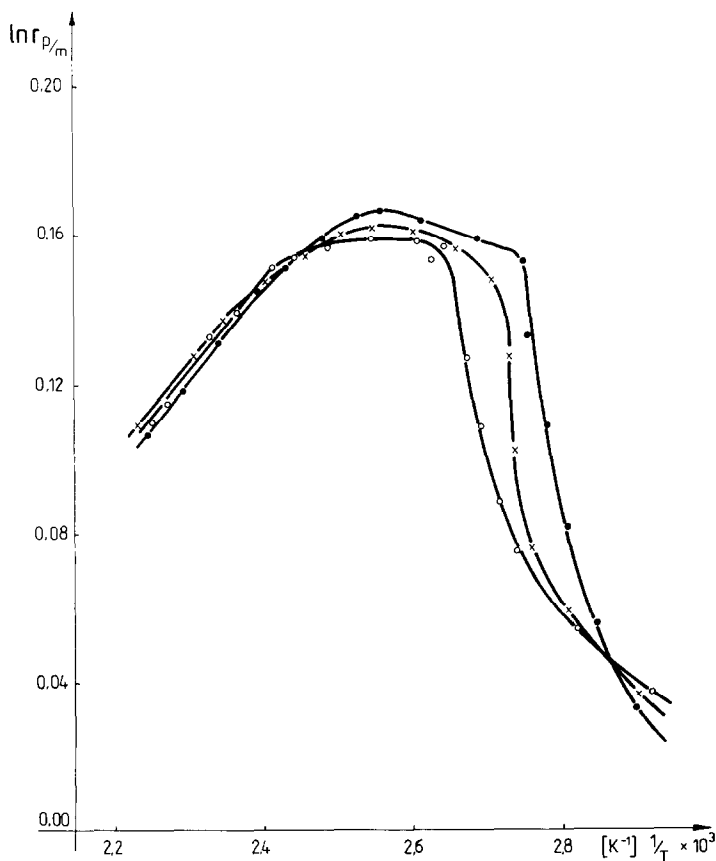
Fig. 2. Temperature dependence of the relative retention times of *p*- and *m*-diethylbenzene for phases II (○), III (●) and V (×).

the carrier gas (argon) was varied from 8 to 50 cm^3/min. Portions of about $1.5 \cdot 10^{-4}$ mm^3 of the mixture of n-octane, n-nonane, n-decane, n-undecane, n-dodecane and n-tridecane were injected into the column. The retention times of the compounds were measured with a stop-watch, the flow-rate of the carrier gas at the column outlet with a bubble flow meter, the pressure at the column inlet with a mercury manometer and atmospheric pressure with a barometer. The calculated heights equivalent to a real plate (HERP) were presented in the form of a relationship to the linear carrier gas flow-rate[16].

RESULTS AND DISCUSSION

Selectivity

Figs. 2 and 3 show variation of the relative retention times of p- and m-diethylbenzene with temperature. The highest relative retention times were obtained
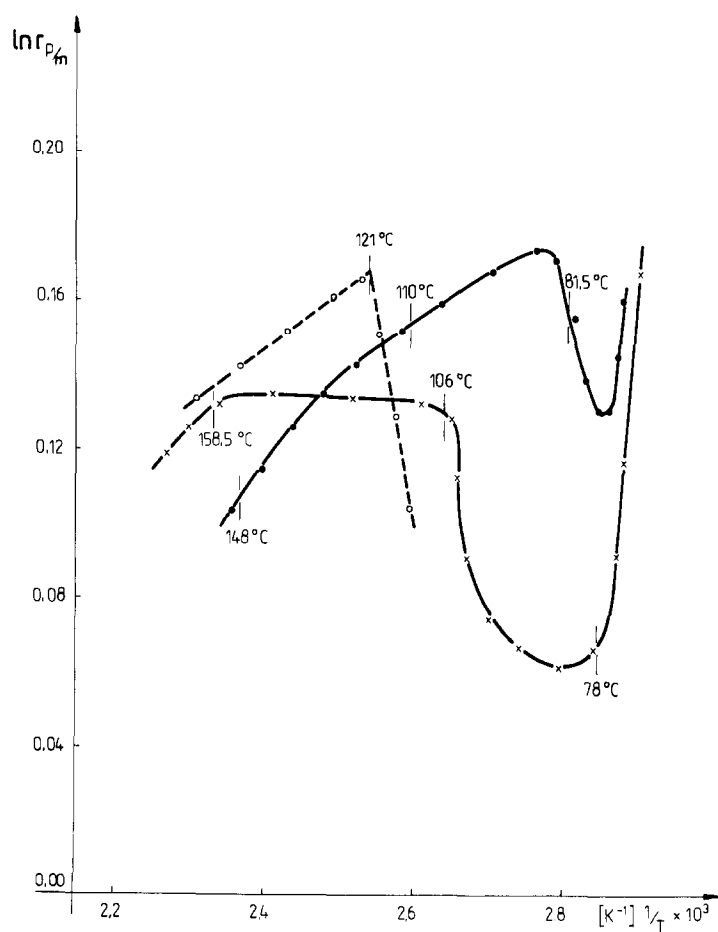

Fig. 3. Temperature dependence of the relative retention times of p- and m-diethylbenzene for phases I (○), IV (×) and VI (●). The dashed line denotes to the relationship obtained when the column was cooling.

for the smectics A and nematics of phases II, III and V. In the smectic B temperature range the selectivity of these compounds is markedly lower (Fig. 2). The plot allows one to determine approximately the limits of the particular types of mesophases, but they are not sharp.

It was expected that the mixture of compounds II and III would show high selectivity, as it is known that the separating properties of mixed phases follow the properties of their components[17]. It can be seen, however, from the phase plot in Fig. 1 that the maximum broadening of the mesophase, occurring when the weights of the components in the mixture are equal, is small and therefore the increase in selectivity is also small.

Fig. 3 shows the variation of the logarithm of the relative retention times of *p*- and *m*-diethylbenzene with temperature for stationary phases I, IV and VI. These phases have lower selectivities than II, III and V, but the numerical values are of a similar order. Nevertheless, the plots differ considerably. With compound IV all the phase transitions are seen distinctly, whereas with compound I only the transition from the solid to smectic B is visible. For phase VI the phase transitions are shifted with respect to the corresponding temperatures measured thermo-optically.

For smectic B the selectivities of phases II, III, IV and V are low. In the smectic B temperature range, for phases II and IV we observed deviations from linearity of the variation of the retention index with temperature with respect to *m*-diethylben-zene (Fig. 4), whereas for phase III and the mixture of phases II and III deviations occurred with respect to both isomers (Fig. 5). In smectic B the molecules are parallel and arranged in layers[18] and inside these layers ordered systems similar to those encountered in the solid occur. The molecules are arranged vertically or slanting with respect to these layers and are ordered hexagonally, *i.e.*, their centres of gravity are located at the vertices of regular hexagons. As a result, the molecular layer of smectic B is similar to a two-dimensional crystal that distinguishes poorly between the *meta*
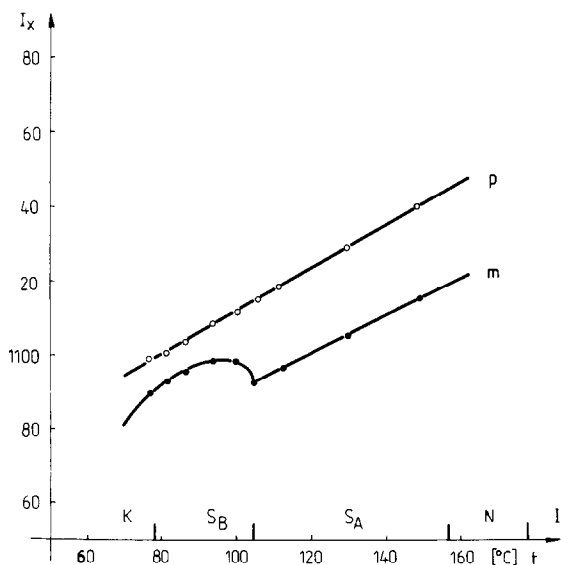

Fig. 4. Temperature dependence of the retention indices of *p*- and *m*-diethylbenzene for phase IV.
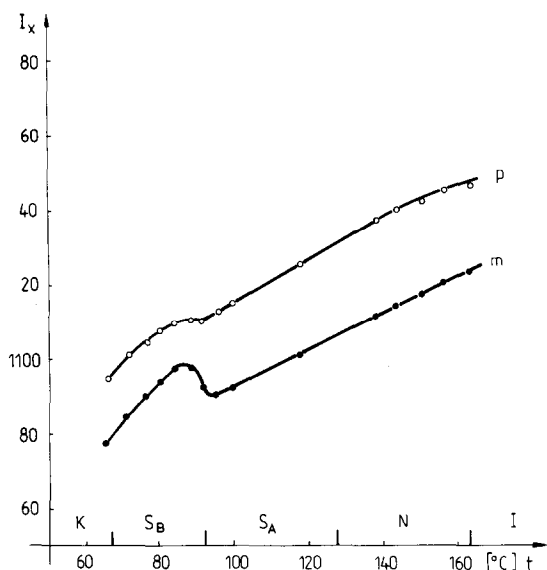
Fig. 5. Temperature dependence of the retention indices of *p*- and *m*-diethylbenzene for the mixed phase V (II + III).

and *para*-isomers, chiefly because of the increased solubility of the *meta* isomer resulting in an increase in its retention index and causing a deviation from linearity of the $I_x = f(t)$ plot. This relates to phases II and IV; an example for phase IV is shown in Fig. 4. With phases III and V this interaction is also observed with respect to the *para* isomer (Fig. 5), although with the *meta* isomer it is more pronounced.

In the nematic mesophase range and in the transition to the isotropic liquid of phases II, III and V a deviation from linearity occurs for the *para* isomer in the opposite direction to that observed for smectic B, which is shown in Fig. 5. This effect probably also occurs with phase IV, but measurements were not made in the proper temperature range. In no instance was such a deviation observed for the *meta* isomer in the temperature range corresponding to the transition from the nematic to the isotropic liquid.

The effects described above, were not observed with phases I and VI. Although measurements were not made for phase I in the region of the N–I transition, no deviations were observed in the smectic range. This may be related to the monotropic character of smectics A and B. With phase VI the existence of only one smectic species (probably poorly ordered) and a cholesteric is the cause of the lack of deviations in the $I_x = f(t)$ plot (Fig. 6).

The selectivity of smectic A was found to be higher than that of smectic B (Figs. 2 and 3). In smectic A the molecules are arranged vertically to the layers but they cannot migrate in the layers[18]. The centres of gravity of the molecules are distributed in a disordered manner on the plane passing through the middle of the layer. In view of this lack of order, every molecular layer resembles a two-dimensional liquid. The increased selectivity of this liquid compared with smectic B is related to the increased (but varying) solubility of the chromatographed compounds in the liquid, account being taken of the differences due to changes in temperature. The
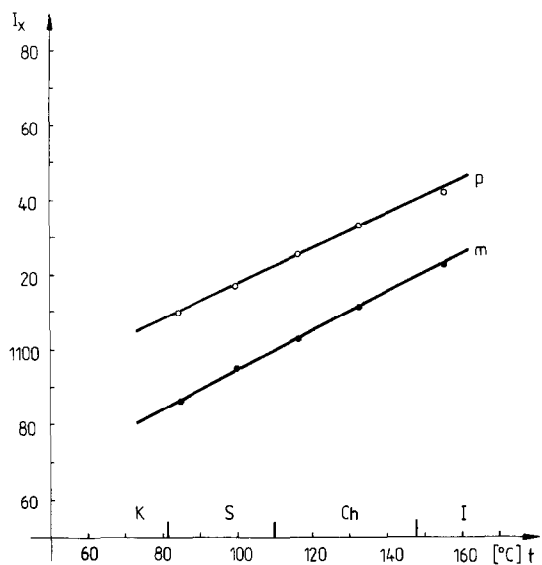
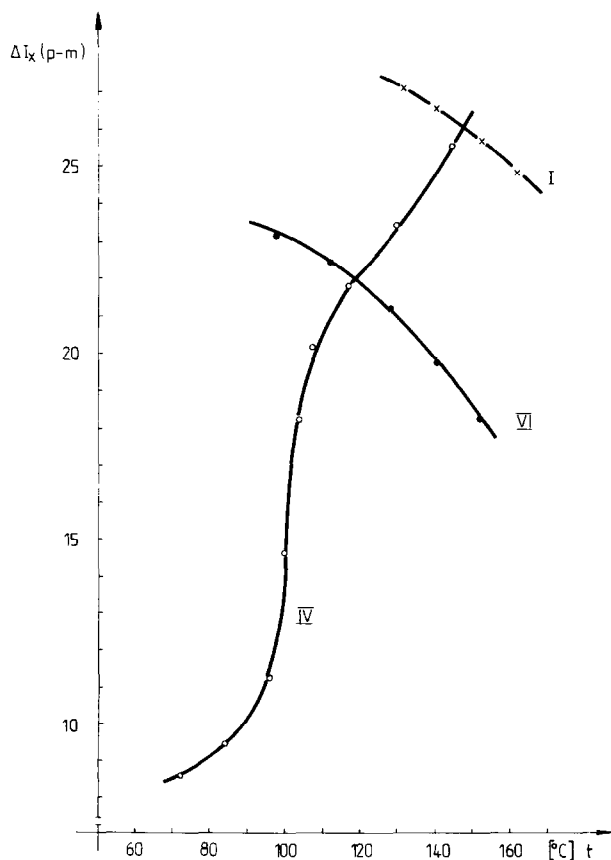Fig. 6. Temperature dependence of the retention indices of *p*- and *m*-diethylbenzene for phase VI.

Fig. 7. Dependence of the differences in the retention indices of *p*- and *m*-diethylbenzene on temperature for phases I, IV and VI.

selectivity of smectic A is greatest at higher temperatures in the range in which it exists, as the ordering is then lower than at lower temperatures and closer to the nematic one.

In the nematic the molecules are ordered parallel but the centres of gravity are distributed at random[18]. As in other phases, the ordering of the nematic is the greater the lower is its temperature. In the nematic, as distinct from the smectic, the highest selectivity is obtained at temperatures close to the melting point, *i.e.*, at the highest ordering. Hence the selectivity of nematic phases is greater at lower temperatures and decreases with increasing temperature (Figs. 2 and 3).

In a cholesteric liquid crystal (phase VI), the molecules are arranged horizontally in parallel layers, but the layers are twisted with respect to each other, which gives spiral systems that have interesting optical properties. Such an arrangement of molecules reveals a low capacity to distinguish between positional isomers[19,20]. As in nematics, the selectivity of cholesterics decreases with increasing temperature (Fig. 3).

The selectivities of the mesophases of the tested stationary phases obtained from cyclohexane derivatives can be arranged in the following order: $S_B < Ch < S_A \approx N$.
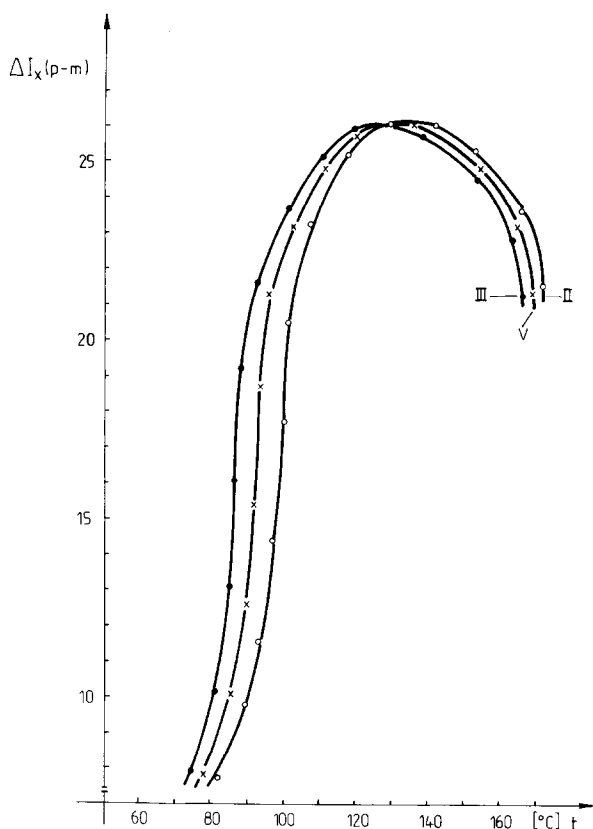

Fig. 8. Dependence of the differences in the retention indices of *p*- and *m*-diethylbenzene on temperature for phases II, III and V.

For all phases the differences in the retention indices of *p*- and *m*-diethylbenzene vary non-linearly with varying column temperature (Figs. 7 and 8). They decrease for phases I and VI and increase for phase IV over the whole temperature range tested. With phase VI, this refers to the whole mesophase region. In phases II, III and V the differences of the retention indices reach their maximum for the smectic A–nematic phase transition.

Polarities

Measurements were not made for phase I as its melting point is higher than 120°C and its supercooling was unstable, which made it impossible to obtain reproducible retention times at 120°C.

The retention indices obtained for the test substances are summarized in Table II. It can be seen that the tested liquid crystal phases are of low polarity. Their polarity is lower than that of many other liquid crystals, which on average have medium polarity[17]. The polarity of the mixture of phases II and III is intermediate between those of the individual components. The lowest polarity was found for phase IV, despite the presence in its molecule of an ether bond. It seems that the presence of the alkoxy group is the cause of the distinct differences between the properties of this phase and those of phases II and V, which contain an alkyl chain.

TABLE II

POLARITY OF STATIONARY PHASES II–VI CHARACTERIZED BY THE USE OF RETENTION INDICES

Test substance	Retention index				
	II	III	IV	V	VI
Benzene	734.7	746.1	731.5	743.0	751.3
1-Butanol	719.9	749.1	699.5	740.1	739.8
2-Pentanone	734.1	761.4	715.2	749.5	753.9
1-Nitropropane	834.3	854.2	817.2	843.6	855.3
Pyridine	868.1	954.9	848.2	912.3	902.6
m-Xylene	953.6	959.7	951.7	956.1	963.6
p-Xylene	964.7	969.4	962.8	966.6	970.0

Efficiency

The dependences obtained of the HERP on the linear carrier gas flow-rate are presented in Fig. 9. The HERPs are fairly high and the columns have relatively low efficiencies. The highest optimal efficiencies were obtained for the columns containing phases II, III and IV, for which the HERPs are about 0.6 mm. The lowest efficiency was shown by the column containing phase I, whose optimal HERP was 0.9 mm, which is distinctly lower from those of the columns containing the other stationary phases. The mass transfer resistance is probably greater in phase I than in the other phases, which may be related to its different chemical structure. The efficiency of the mixed phase V is intermediate between those of its components and under optimal conditions reaches 0.62 mm.

The optimal values of the linear flow velocity lie between about 16 and 19 cm/sec.
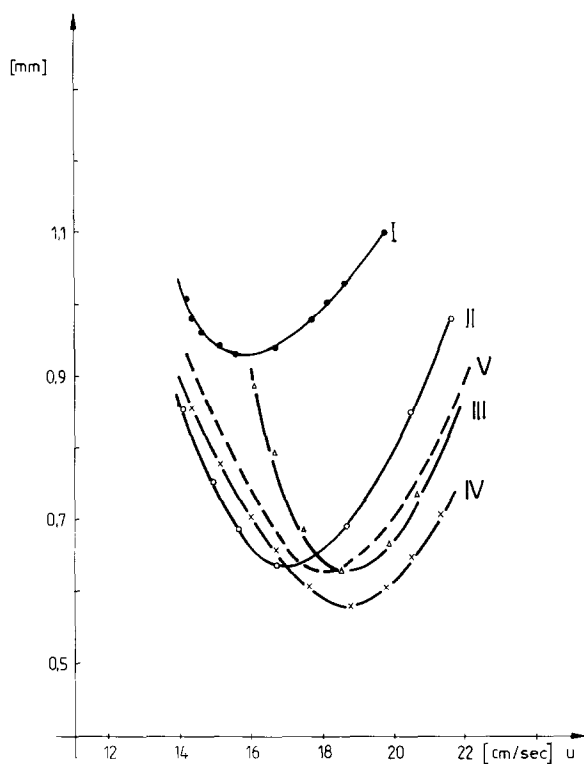
Fig. 9. Dependence of the real plate height on the carrier gas flow-rate for phases I–V.

The cyclohexane derivatives give, like other groups of liquid crystalline stationary phases, lower column efficiencies than conventional stationary phases. Hence the good separating effects of liquid crystalline stationary phases are related to their significant selectivity.

CONCLUSIONS

Liquid crystalline stationary phases containing a cyclohexyl ring in their molecule have a lower selectivity towards disubstituted benzene isomers than those in which the cyclohexyl ring is replaced with a benzene ring.

Phases II–VI showed no signs of bleeding at temperatures up to about 10°C below the point of transition to the isotropic liquid. Phase I was thermally stable up to about 160°C.

Phases II–VI do not supercool. Compound I melts at 154.5°C, and when supercooled yields a smectic phase down to 121°C. A further decrease in temperature led to a rapid decrease in the retention time of the chromatographed compounds, which indicates that further supercooling is instable.

The low polarity of the tested phases leads to a preference for their application in the chromatographic analysis of non-polar compounds. The selectivity of the

tested phases decreases, depending on the molecular structure or rather on the type of terminal substituent, in the order alkyl > isoalkyl > alkoxy.

This study extends our knowledge of liquid crystal stationary phases. The deviation of the retention indices from linearity in the smectic B range and at the nematic to isotropic liquid transition and the appearance of a maximum in the difference in the retention indices in the smectic A to nematic transition region are very interesting phenomena.

ACKNOWLEDGEMENT

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