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EFFECT OF LATERAL SUBSTITUENTS ON THE PROPERTIES OF LIQUID CRYSTAL MOLECULES AS STATIONARY PHASES IN GAS CHROMATOGRAPHY

ANNA ZIÓŁEK, ZYGFRYD WITKIEWICZ* and ROMAN DĄBROWSKI
Institute of Chemistry, Military Technical Academy, 01 489 Warsaw 49 (Poland)
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SUMMARY

The properties of liquid crystalline azo compounds with lateral substituents (CH_3, CN, Cl) have been tested from the point of view of their suitability as stationary phases in gas chromatography. The tested properties were compared with those of the unsubstituted compounds. The study consisted in comparing the retention properties of the test substances on the stationary phases and determining their selectivity and the efficiency of the columns containing these phases. It was found that minor changes in the liquid crystal molecular structure affect the properties of the liquid crystalline stationary phases. The properties of the liquid crystal with respect to the test substance depend on the kind of substituent and its position. The interactions of liquid crystal molecules with the same substituents depend on the kind of substance chromatographed.

INTRODUCTION

More than a decade has elapsed since liquid crystals were first successfully applied as stationary phases in gas chromatography. In this period many papers have been published on with the separating properties of those phases. Studies have also been devoted to the effect of the support on the physico-chemical properties of the liquid crystal layers and their separating properties. The knowledge on liquid crystalline stationary phases has been summarized in surveys[1–7].

Analysis of the studies described so far shows that we lack sufficient knowledge to be able to explain the relationship between the molecular structure of the liquid crystal and its separating properties, account being taken of the effect of the support. It is known that different liquid crystals, the mesophases of which have the same structure, may show different separating properties towards the same mixtures. It can be concluded, therefore, that the molecular structure of the liquid crystal plays an important role in the separation process taking place on a liquid crystalline stationary phase.

A knowledge of the relationship between the molecular structure of the liquid crystal and its separating properties would allow a more rational choice of liquid

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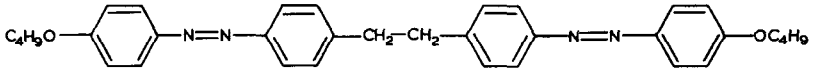
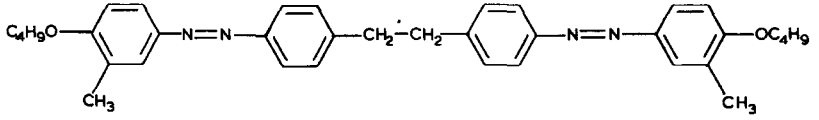
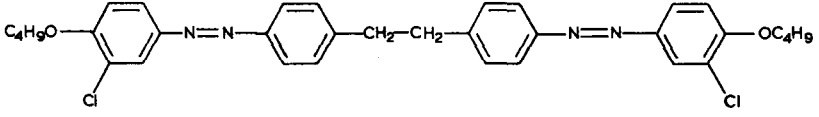
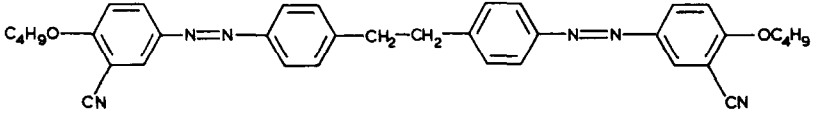
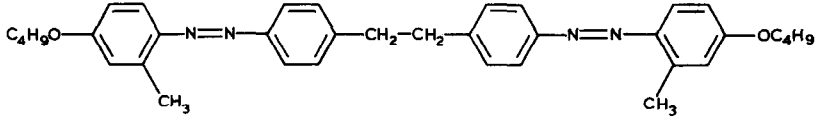
TABLE I

STRUCTURES OF STATIONARY PHASES AND PHASE TRANSITION TEMPERATURES

Phase	*Formula*	*Phase transition temperature (°C)*				
		K	→ *S*	→ *N*	→ *I*	
I		201			310	
II		193			253	
III		179		197	256	
IV		197		212	283	
V		116			229	

crystalline stationary phases for solving different analytical problems. Such knowledge should also contribute to the selection of new methods of synthesis of liquid crystalline stationary phases that would reveal pre-determined parameters and meet the desired requirements.

In this work we studied how the properties of liquid crystalline stationary phases are affected by the simultaneous presence of two lateral substituents in their molecules. Methyl, cyanide and chlorine were used as substituents. Earlier studies concentrated on the effect of single lateral methyl substituents[8,9] and of two chlorine substituents[10] on the chromatographic properties.

EXPERIMENTAL

Column fillings

Liquid crystalline azo compounds, whose synthesis was described earlier[11], were used. Their structures and the phase transition temperatures are given in Table I. Chromosorb W NAW, W AW DMCS and P HMDS were used as supports. The grain size of Chromosorb W NAW and P HMDS was 0.20–0.25 mm and that of Chromosorb W AW DMCS was 0.15–0.20 mm. The liquid crystals were deposited on the support from chloroform solutions by slow evaporation of the solvent under reduced pressure. The real amount of the stationary phase on the support was determined from the decrease in mass on heating the filling to constant weight in an oven at 600°C. The support with the deposited liquid crystal was placed in stainless-steel columns (1 m × 4 mm I.D.) (one column had a length of 1.5 m). The characteristics of the columns are given in Table II.

Measurement procedure

The tests were carried out on a Pye Unicam GCV chromatograph adapted to physico-chemical measurements by connecting a mercury manometer to the injector to permit the measurement of pressure at the column inlet. In all measurements a flame-ionization detector was used. Argon was used as the carrier gas, its flow-rate in measurements of the retention of the test substances being 25 cm^3/min. Prior to use every column was heat conditioned for about 2 h. The conditioning temperature was adjusted so as to prevent bleeding of the stationary phase from the column. In all instances the temperature was lower than the mesophase–isotropic liquid transition point. After the heat conditioning was completed, the column was cooled to ambient temperature, when its heating was started.

The physico-chemical investigations never encompassed the whole mesophase range, but only that part containing the solid–mesophase transition. The tests were started in the solid temperature range (about 20–30°C below the melting point) and ended at a temperature at which the vapour pressure of the stationary phase was sufficiently low to prevent visible bleeding of the stationary phase.

The column temperature was increased by 5°C steps, except for the phase transition regions, where 2°C steps were applied. Before every measurement the column was heat conditioned at the particular temperature for 20 min. At every temperature the flow-rate of the carrier gas was determined and the pressure at the column inlet was read on the manometer; it was assumed that the pressure at the outlet is equal to atmospheric. The dead time was determined at each temperature

TABLE II

COLUMN CHARACTERISTICS

Column No.	*Phase notation*	*Chromosorb support*	*Amount of phase (%)*	*Column length (m)*
1	I	P HMDS	2.20	1.5
2	I	W AW DMCS	1.82	1.0
3	I	W NAW	2.07	1.0
4	II	W AW DMCS	2.13	1.0
5	III	W AW DMCS	2.62	1.0
6	III	W NAW	2.35	1.0
7	IV	W AW DMCS	2.12	1.0
8	V	W NAW	2.05	1.0

by means of methane. The retention time of the test substances was measured with a stop-watch, the mean value from at least two measurements not differing by more than 0.2 sec (for shorter retention times) or 1 sec (for longer retention times) being used for the calculations. When taking measurements in order to determine the retention characteristics, 1:50 solutions in benzene of phenanthrene, anthracene and acridine, and in the case of column 8 1-methylnaphthalene, were injected into the column. Samples of 0.02 μl were injected by means of a 1-μl Hamilton syringe.

The column efficiency was determined from the chromatograms of the test substances obtained at constant temperature at different flow-rates of the carrier gas in the range 10–50 cm^3/min. The measurements were taken at the solid mesophase transition temperature determined chromatographically. In the column efficiency measurements various test substances (benzophenone, naphthalene, 2,3-dimethylnaphthalene and anthracene) were used, depending on the retention time, the partition ratio obtained for the test substance on the given phase and the peak symmetry.

RESULTS AND DISCUSSION

The liquid crystals selected for the tests reveal a nematic (compounds I, II and V) or smectic–nematic (compounds III and IV) ordering in the mesophase region. These compounds have large molecules and, having identical main chains, they differ only as regards the lateral substituents.

It seemed interesting to check how minor differences in the molecular structure affect the properties of the compounds when applied as stationary phases in gas chromatography. Studies of the dependences of the retention times of the test substances on the temperature of the columns, in which the liquid crystals listed in Table I were used as stationary phases, gave relationships typical of liquid crystals, despite their low percentage on the support (see Fig. 1). These relationships reveal a fairly rapid decrease in retention time at temperatures corresponding to the solid state after which, several degrees before the phase transition, an increase is observed. The maximum retention time probably corresponds to the temperature of transition to the mesophase, although this temperature does not completely coincide with that observed thermo-optically. In the mesophase range a subsequent decrease in the reten-

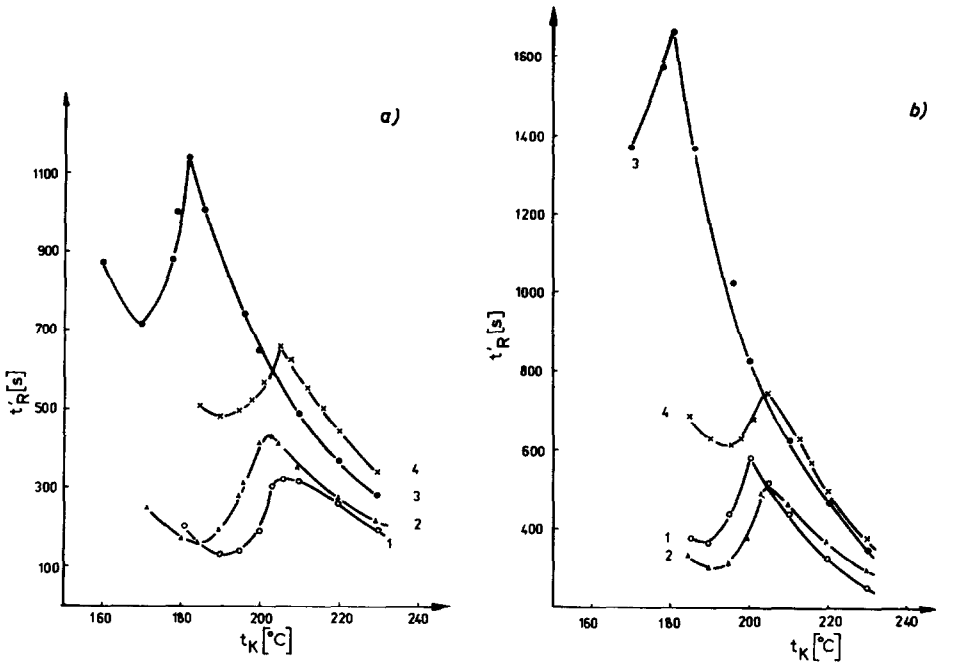


Fig. 1. Variation of the retention time (t'_R) with column temperature (t_K) for (a) anthracene and (b) acridine: curve 1, phase I (column 2); curve 2, phase II (column 4); curve 3, phase III (column 5); curve 4, phase IV (column 7).

tion time with increasing temperature is observed. However, such relationships are not always observed and this depends on the kind of liquid crystal and its amount on the support, and also on the type of support[12–16]. In some instances a relationship non-typical of liquid crystalline phases between the retention time and retention volume and the column temperature is observed. The extreme points characteristic of phase transitions are not observable on the plots.

The temperature of column conditioning has an influence on whether these phase transitions are observed chromatographically or not. This temperature was lower than that of transition to the isotropic liquid with the high-temperature liquid crystalline stationary phases studied. It was not possible to condition the columns at a temperature corresponding to the isotropic liquid, as the liquid crystals tested decomposed at this temperature or showed considerable bleeding. Phase V served as an example, illustrating that the column conditioning temperature influences the character of the relationship between the retention time of the test substance and the column temperature (Fig. 2).

The curve $t'_R = f(t_K)$ (curve 3) for the column that was not subjected to preliminary conditioning has a course typical of liquid crystals and reveals a sharply marked phase transition. This column was subsequently conditioned at a temperature 24°C higher than the liquid crystal melting point, cooled and then the retention time of the test substance was measured as a function of the column temperature. An increase in the retention times is observed in the range of the stationary phase solid state, the value of t'_R being preserved in the mesophase range, however, and the curve

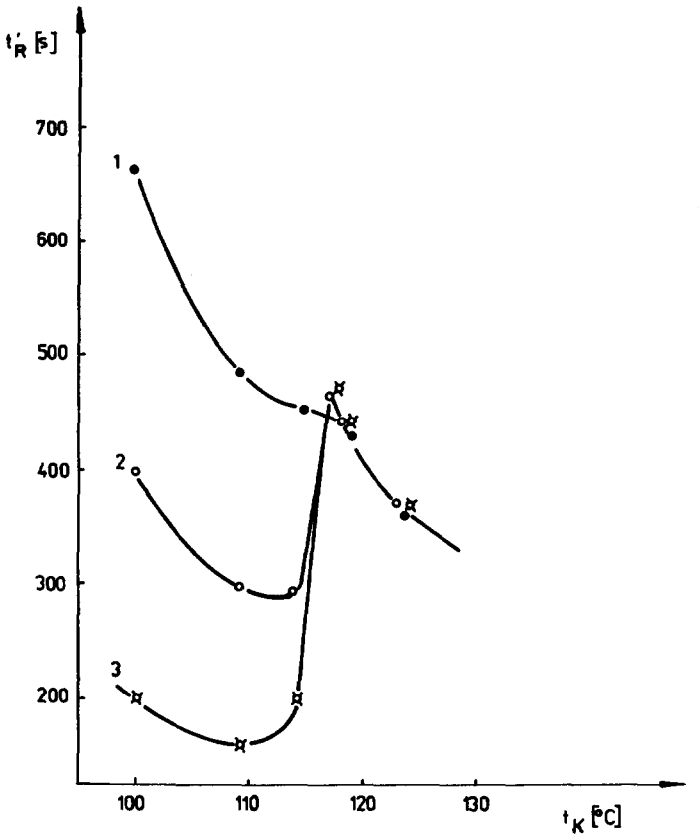


Fig. 2. Variation of retention time of 1-methylnaphthalene on phase V (column 8) with column conditioning temperature: curves 1, 2 and 3, columns conditioned at 220, 143 and 180°C and unconditioned, respectively.

keeping its general character typical of liquid crystals (curve 2). A further increase in the column conditioning temperature had no effect on the value of t'_R up to the moment when the conditioning temperature reached a temperature close to the transition point to the isotropic liquid (curve 1), when a further increase in the retention times in the solid range was observed, together with a decay of the extremes on the $t'_R = f(t_K)$ plot typical of liquid crystalline stationary phases. The plot obtained has an inflection in the phase transition region. These results allow us to conclude that agglomerates of crystals are formed in the course of depositing the phase on the support, which form drops on heating to the melting point. Under these conditions the phase has properties typical of the lack of interactions with the support. An increase in temperature, results in a decrease in the liquid crystal viscosity and a change in the wetting angle. The liquid crystalline phase is then more uniformly distributed over the support surface by capillary and superficial forces, and the number of molecules exposed to the direct action of the support surface increases. This probably influences the way the liquid crystalline substance crystallizes during cooling of the column. The structure produced during crystallization may resemble that re-

vealed by the substance in the mesophase range, provided that the layer of the phase on the support is sufficiently thin. As a result, the effects connected with the reconstruction of the solid crystal structure to the liquid crystalline structure taking place during melting of the substance is avoided and the solubility of the test substance changes only to the extent due to the change in temperature.

In order to determine the effect of the support on the properties of the investigated stationary phases, we measured dependence of the retention time of the test substances on the column temperature for the same phases deposited in similar amounts on Chromosorb W NAW and W AW DMCS. We then plotted the specific retention volume *versus* temperature, $V_g = f(1/T_K)$. The changes in the specific retention volume due to the change of support were found to depend on the molecular structure of the liquid crystalline stationary phases. With phase I we observe significant differences in the values of the specific retention volume in the region preceding the solid mesophase transition (Fig. 3); on transition to the mesophase these differ-

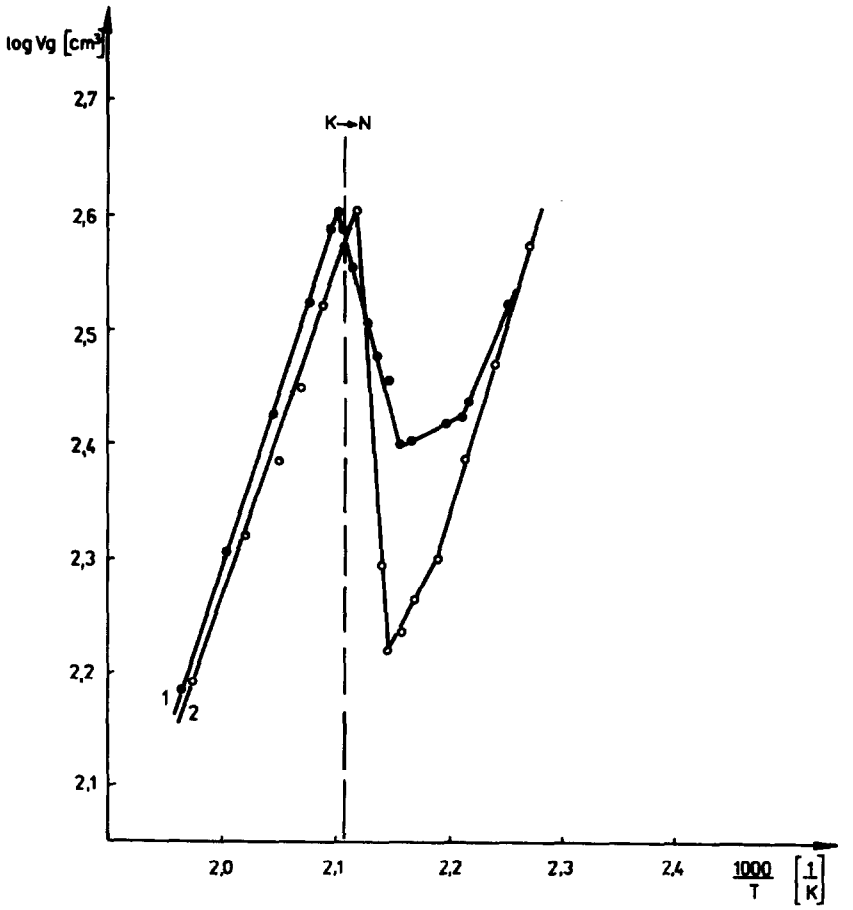


Fig. 3. Variation of the specific retention volume of anthracene on phase I with column temperature: curve 1, phase deposited on Chromosorb W AW DMCS (column 2); curve 2, phase deposited on Chromosorb W NAW (column 3).

ences decrease. The values of the specific retention volumes at the temperature of transition to the mesophase are the same for both supports. In the mesophase range higher values of the specific retention volume were obtained when the phase was deposited on Chromosorb W AW DMCS. In that case the temperature at which we observe the maximum specific retention volume is higher than the phase transition point determined thermo-optically, being higher for Chromosorb W AW DMCS than for Chromosorb W NAW. With phase III, which contains in its molecule a lateral substituent (Cl), we observe significant differences of the specific retention volume over the whole temperature range studied. Higher retention values were found when the phase was deposited on Chromosorb W NAW (Fig. 4). The phase that has a smectic–nematic ordering in the investigated temperature range reveals no changes in the linearity of the relationship $V_g = f(1/T_K)$ in the region of the smectic–nematic transition point. By comparing the specific retention volumes obtained for anthracene chromatographed on phases I and III deposited on the same support we found that higher retention values over the whole temperature range studied are obtained for phase III. This indicates that the chromatographed substance is retained longer on the phase with a lateral substituent than on the phase without such a substituent.

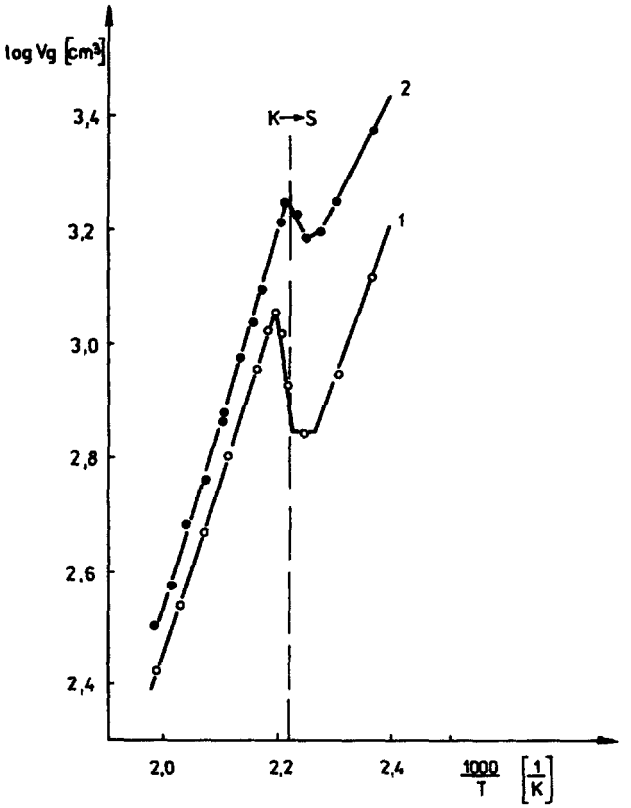


Fig. 4. Variation of the specific retention volume of anthracene on phase III with column temperature: curve 1, phase deposited on Chromosorb W AW DMCS (column 5); curve 2, phase deposited on Chromosorb W NAW (column 6).

The selectivity of the tested stationary phases was determined for two pairs of test substances: (i) differing in the shape of molecules (anthracene–phenanthrene) and (ii) differing in polarity (acridine–anthracene). It is interesting that the courses of the $r_{1/2} = f(t_K)$ curves obtained for these two pairs of substances are different (Figs. 5 and 6). For the pair anthracene–phenanthrene chromatographed on phases I and II (having solely a nematic ordering in the mesophase range) the value of $r_{1/2}$ increases in the vicinity of the K → N phase transition, the maximum occurring at a temperature several degrees higher than that of the phase transition found thermo-optically. The transition to the nematic phase is revealed by only a small inflection on the $r_{1/2} = f(t_K)$ plot. The changes in the $r_{1/2}$ value for the pair anthracene–phenanthrene chromatographed on phase IV are small over the whole temperature range investigated. A weak maximum appears in the smectic phase range, but considerably shifted (11°C) from the K → S phase transition temperature determined thermo-optically.

The shape of the $r_{1/2} = f(t_K)$ relationship for the acridine–anthracene pair is similar to that obtained on non-liquid crystalline phases (Fig. 6). There is no maximum on transition to the mesophase, but a rapid decrease in the $r_{1/2}$ value is observed at temperatures several degrees above the solid–mesophase transition. With phases

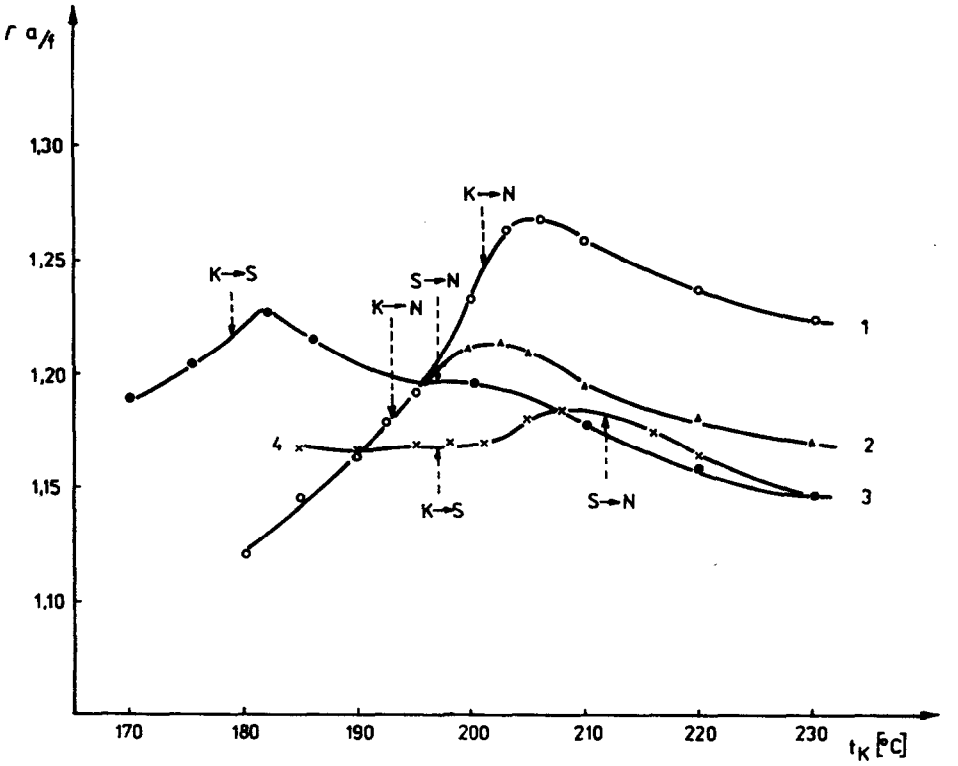


Fig. 5. Variation of relative retention times of anthracene and phenanthrene with column temperature: curve 1, phase I (column 2); curve 2, phase II (column 4); curve 3, phase III (column 5); curve 4, phase IV (column 7).

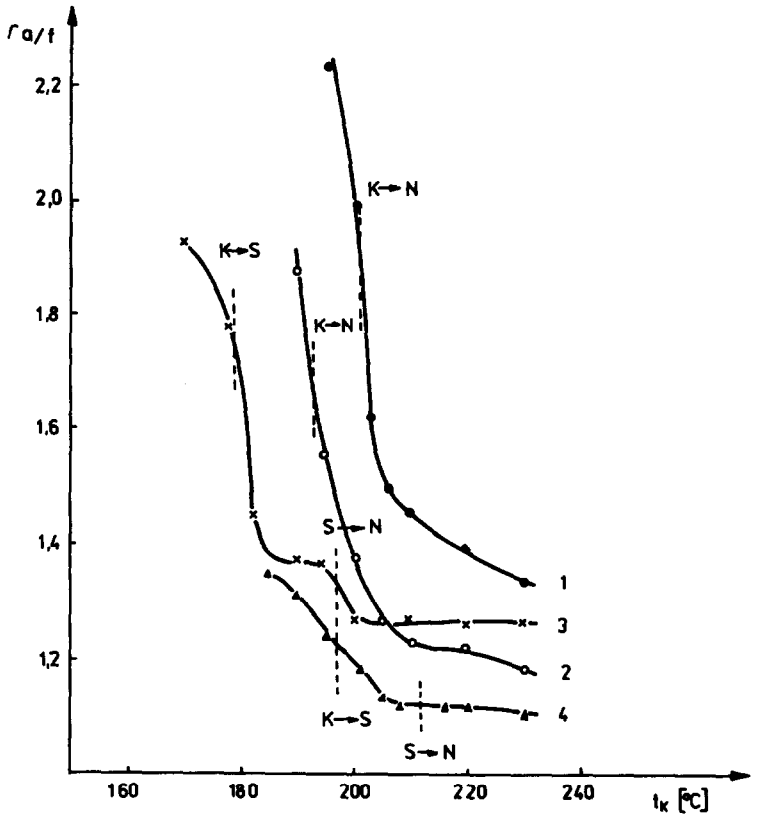


Fig. 6. Variation of the relative retention times of acridine and anthracene with column temperature: curve 1, phase I (column 2); curve 2, phase II (column 4); curve 3, phase III (column 5); curve 4, phase IV (column 7).

I and II a further increase in temperature has only a minor effect on the relative retention times. Phase III reveals a repeated decrease of the $r_{1/2}$ value in the vicinity of the S → N transition temperature, after which the relative retention times remain virtually constant in the nematic phase range. The changes in the $r_{1/2}$ value due to transition to the mesophase are fairly small with phase IV, as for the phenanthrene–anthracene pair. Here also we observe virtually constant $r_{1/2}$ values in the nematic phase range.

The interactions of the stationary phases with acridine and anthracene are different for a particular stationary phase in different temperature ranges, as can be seen from the retention time *versus* temperature plot in Fig. 1. In both instances there is an increase of the t'_R value at the transition to the mesophase, which is connected with the increased solubility in that phase. At the same time the plots of variations in relative retention time for the acridine–anthracene pair seem to indicate that the change in interaction related to the shape of the molecules is the same for both substances. The acridine and anthracene molecules do not differ in shape but only in their polarities and boiling points. Therefore, no additional differences in the in-

teraction of the stationary phase with acridine and anthracene due to differences in the molecular shape are observed on transition to the ordered mesophase. Hence, in contrast to the anthracene–phenanthrene pair, no increase in the relative retention times is detected. When analysing the $r_{1/2} = f(t_K)$ relationship for the acridine–anthracene pair, one should not neglect the effect of the differences in their polarities or their boiling points (acridine 346°C, anthracene and phenanthrene 340°C). The effect of polarity is greatest in the range of transition from the solid to the smectic or nematic phase.

It seems that the increase in the solubility of the stationary phases of low polarity on transition to the mesophase is greater for non-polar anthracene than for polar acridine. As a result, when the absolute retention times of both substances increase, their relative retention times decrease rapidly in the solid–mesophase transition region and settle in the nematic range at a certain level characteristic of the phase. The adsorption of polar acridine on the support may not be neglected. In the solid temperature range of the stationary phase, when the amounts deposited were small the proportion of adsorption on the support may be significant. On transition of the liquid crystalline stationary phase to the mesophase the number of free sorption centres on the support decreases owing to the better coverage of the support surface by the phase. The proportion of sorption on the support in the process of chromatographing acridine also decreases and its absolute retention times are thereby lowered. The increase in the absolute retention times of acridine, as a result of changes in the dissolution and sorption process, is smaller than that of anthracene, and this in turn causes a decrease in the relative retention times. The higher values of the relative retention times obtained for the acridine–anthracene pair compared with the anthracene–phenanthrene pair are due not only to the differences in polarity but also to the differences in the boiling points of the first two substances. The above discussion confirms the very large effect of the shape parameter of the chromatographed molecules in the process of separation on liquid crystalline stationary phases, although the final effect of this process is the result of the action of a whole range of parameters such as the boiling points of the chromatographed substances, their polarity and the polarities and the structure of the stationary phases, which will be discussed below.

Comparison of the results obtained on the selectivity of the stationary phases showed that the relative retention times are highest for both the anthracene–phenanthrene and acridine–anthracene pairs when they are chromatographed on phase I, which has no lateral substituents. The phases that contain such substituents in their molecules show lower selectivity with respect to the substances studied. The effect of the kind of substituent is not unique, and depends on the type of substance being chromatographed. The relative retention times for the anthracene–phenanthrene pair are higher in the mesophase range on phase II (with a CH_3 group) than on phases III and IV (with a Cl and a CN group, respectively). As regards the acridine–anthracene pair, phase IV (with a CN group) shows the lowest selectivity, the selectivity of phase III being greater than that of phase II in the nematic range. The observed effects disagree with the predictions if only the polarity due to the polarity of the substituents ($CN > Cl > CH_3$) is considered. In addition to polarity, electron donor–electron acceptor interactions with the phases, which may be greater with anthracene than acridine, should be taken into account.

The lower selectivity of the phases with lateral substituents is probably due to the increased intermolecular distances in the mesophase, which weaken the steric effects responsible for the phase selectivity. The differentiation of the selectivities of the phases with lateral substituents towards phenanthrene and anthracene is small, probably owing to the small differences in the intermolecular distances in the phases and also to the small effect of phase polarity on the non-polar hydrocarbon test substances.

With acridine and anthracene, the presence of lateral substituents, affecting the polarity of the stationary phase molecules, leads to the appearance of differences in the interactions of the particular phases with polar acridine, which in turn produces a greater differentiation of selectivity of the phases with lateral substituents towards the acridine-anthracene pair. The different behaviour of the stationary phases with respect to the different chromatographed substances makes it possible to explain the differences between our results and those of other workers[8–10], who observed an increase in the selectivity of phases with lateral substituents as compared with unsubstituted phases. Also, the compared phases did not always belong to the same group[10]. In our investigations we also observed cases when the phases with lateral substituents showed better separating properties towards certain chromatographed substances than the phases without substituents[17].

It has been found that the selectivity of the tested phases depends on the kind of support used. Some examples are shown in Figs. 7 and 8. Higher relative retention

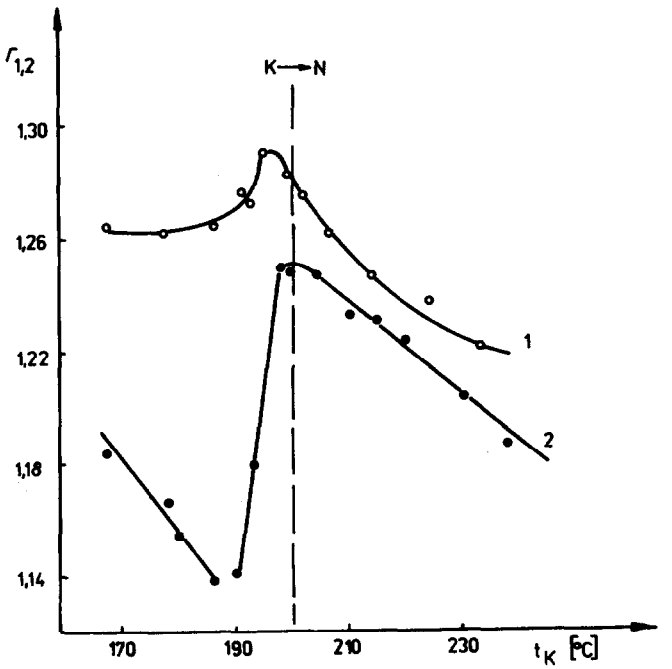


Fig. 7. Variation of the relative retention times of anthracene and phenanthrene with column temperature: curve 1, phase I on Chromosorb W AW DMCS (column 2); curve 2, phase I on Chromosorb W NAW (column 3).

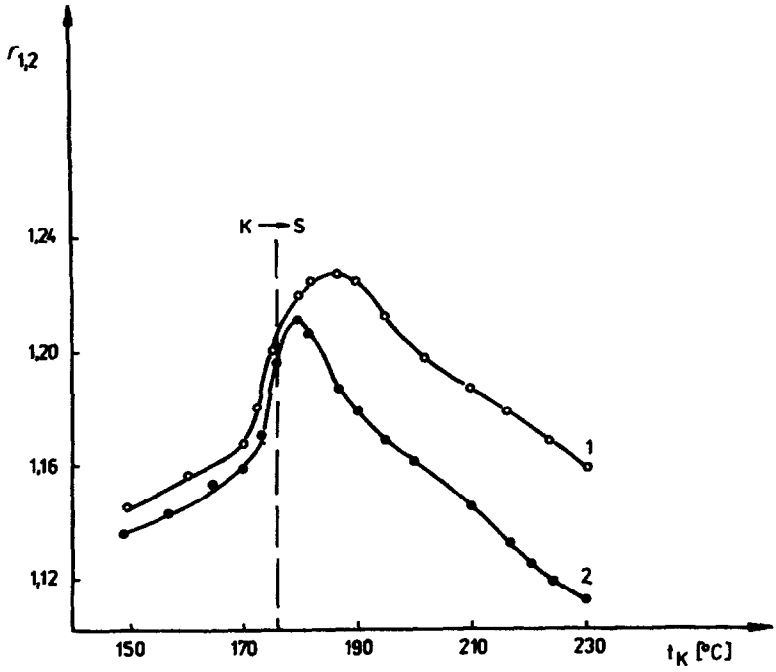


Fig. 8. Variation of the relative retention times of anthracene and phenanthrene with column temperature: curve 1, phase III on Chromosorb W AW DMCS (column 5); curve 2, phase III on Chromosorb W NAW (column 6).

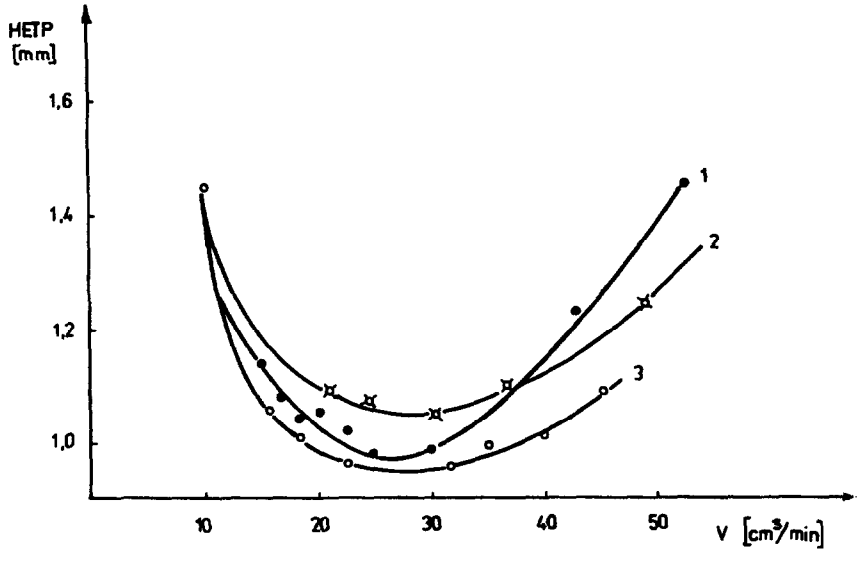


Fig. 9. Variation of HETP with carrier gas flow-rate: curve 1, phase III (column 6), benzophenone as test substance, column temperature 178°C; curve 2, phase I (column 3), anthracene as test substance, column temperature 203°C; curve 3, phase V (column 8), naphthalene as test substance, column temperature 119°C. The column temperatures correspond to the solid–mesophase transitions.

times both for phase I (without a lateral substituent) and phase III (with chlorine in the lateral position) were obtained when the phases were deposited on Chromosorb W AW DMCS.

The efficiencies of the columns tested were determined by calculating the height equivalent to a theoretical plate (HETP) and expressing it as a function of the carrier gas flow-rate (Figs. 9 and 10) and column temperature (Fig. 11). The test substances were selected so that $5 < k' = t'_R/t_m < 10$. Analysis of the dependence of HETP on the carrier gas flow-rate showed that the optimal flow-rates allowing the highest column efficiency to be obtained lie in the range 25–35 cm^3/min. In this range the efficiency of the tested columns varied only slightly.

The column efficiency depended, however, on the kind of stationary phase and support used. Examples are shown in Figs. 9 and 10. The efficiency of the columns in which compounds with lateral substituents were used as stationary phases in the range of optimal carrier gas flow-rates is higher than that of the column with compound I (Fig. 9). Replacement of Chromosorb W NAW with Chromosorb W AW DMCS lowered the column efficiency, whereas the application of Chromosorb P HMDS as a support resulted in increased efficiency, the optimal flow-rate of the carrier gas being shifted towards higher values (Fig. 10) (the carrier gas flow-rate was measured with a bubble flow-meter at the outlet of the column). In the cases studied, greater selectivity was obtained for the phases deposited on Chromosorb W AW

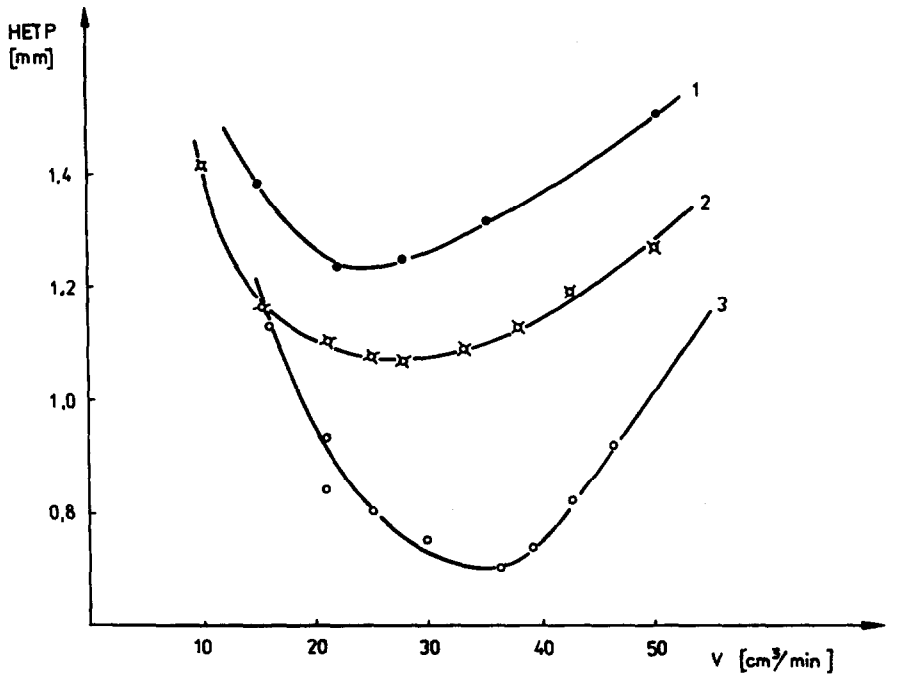


Fig. 10. Variation of HETP with carrier gas flow-rate for columns with phase I on various supports: curve 1, Chromosorb W AW DMCS (column 2), anthracene as test substance; curve 2, Chromosorb W NAW (column 3), anthracene as test substance; curve 3, Chromosorb P HMDS (column 1), benzophenone as test substance. The column temperature was 203°C in all instances.

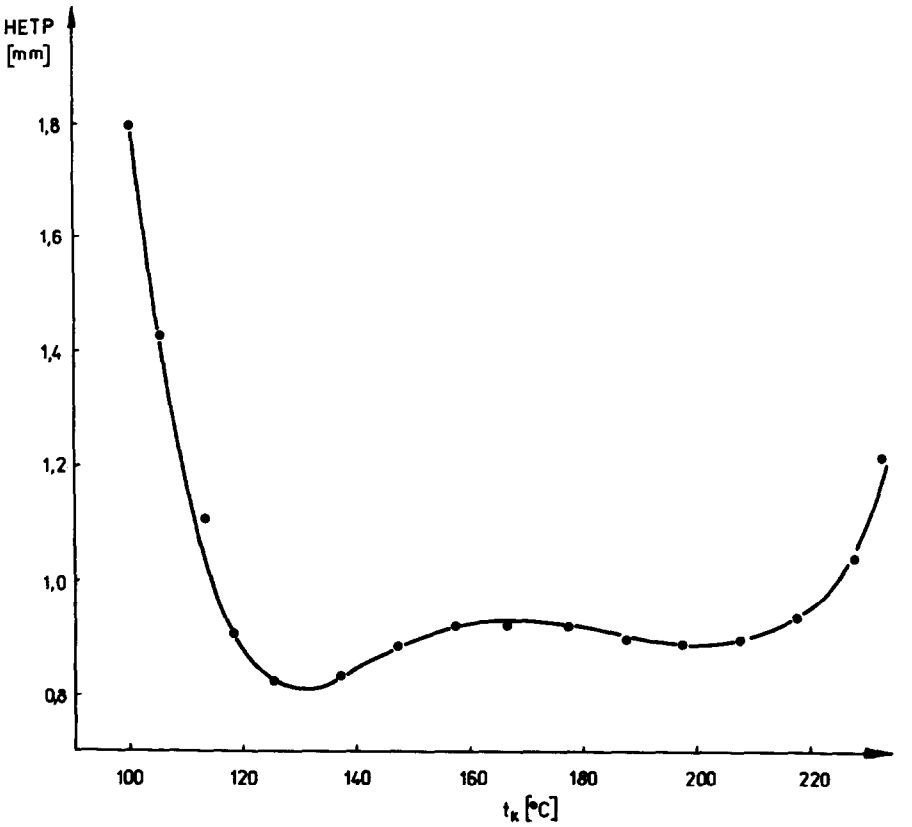


Fig. 11. Variation of HETP with column temperature: phase V (column 8), 2,3-dimethylnaphthalene as test substance, argon flow-rate 25 cm^3/min.

DMCS, the column efficiency then being lower. This suggests that the coverage of the support by the phase is less uniform and hence the effect of the support interferes less with the mesophase structure, which favours higher selectivity of the stationary phase but at the same time increases the mass transfer resistance in that phase.

The studies of the dependence of HETP on column temperature showed (Fig. 11) that the lowest HETP values are obtained at the solid–mesophase transition temperature. In the solid range the HETP value decreases with temperature, whereas in the mesophase range a gradual increase in HETP takes place, beginning from the phase transition temperature. The column efficiency for the tested stationary phases remained almost constant in the mesophase range and began to decrease near the transition point to the isotropic liquid. Such a course of the relationship is an advantage of liquid crystalline stationary phases, which show their greatest separating ability in the mesophase temperature range. The determined column efficiencies were fairly low in all instances. The minimum HETP was about 1 mm.

CONCLUSIONS

The results obtained allow us to conclude that even small changes in the liquid

crystal molecular structure cause significant differences in the behaviour of liquid crystalline stationary phases.

Introduction of a lateral substituent into the stationary phase molecule lowers the selectivity of the phase towards the test substances investigated. The differences in the selectivity of the phases due to the introduction of a substituent depend on the kind of substituent and the type of substance being chromatographed. When the substances do not differ as regards polarity (anthracene–phenanthrene), the kind of substituent in the stationary phase molecule is of less importance than when substances of different polarity (acridine–anthracene) are involved.

The tests confirm the conclusion that the increased selectivity on passing to the mesophase is closely related to the difference in the shapes of the molecules of the substances being chromatographed, although it seems that with polar substances (both the phases and the chromatographed substances) electron factors, including donor–acceptor ones, are significant.

An important role in the chromatographic process is played by the kind of support used, which affects the specific retention volume, the phase selectivity and the column efficiency. This effect, however, is not unique and depends on the kind of liquid crystalline stationary phase involved.

From the above considerations, it can be seen that the structure of the liquid crystal molecule, which controls the interactions of the phase with the chromatographed substance and support, is largely responsible for the efficiency of the chromatographic process on liquid crystalline stationary phases.

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