EFFECT OF THE SUPPORT SURFACE ON THE STRUCTURE OF THE FILM OF LIQUID CRYSTALLINE STATIONARY PHASE

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SUMMARY

It has been found that the chromatographic properties of the Chromosorb P NAW–p-butyl-p'-hexanoylazobenzene system depend largely on the thickness of the liquid crystal film. Modification of the liquid crystal properties by the support surface takes place to a distance of about 2 nm from the surface. The modified liquid crystal layer reveals a selectivity with respect to n-octane and toluene different from that of the liquid crystal in the bulk phase.

INTRODUCTION

Liquid crystalline stationary phases are widely used in gas chromatography[1–3]. They feature universal stationary phase properties and can be used for separating complex mixtures of polar and non-polar compounds and also isomers. The possibility of using high-temperature liquid crystalline stationary phases in the chromatographic analysis of aromatic polynuclear hydrocarbons deserves special emphasis[4–6].

The exceptional physico-chemical properties of liquid crystals are manifested in the properties of the liquid crystalline stationary phase–support system. These properties depend not only on the structure of the mesophase and the liquid crystal molecule but also on the amount of the liquid crystal on the support and on the type of the latter. The properties of the system produce, depending on the column temperature, two kinds of changes in the retention values, viz., revealing or not revealing phase transitions[7].

Vetrova and co-workers[8],[9] showed that a thin film of liquid crystal deposited on the surface of an active adsorbent is significantly affected by the surface. This influence is revealed by the extension of the range in which the liquid crystalline phase exists and, in practice, when the liquid crystal is used as the stationary phase in partition gas chromatography, by the extension of the temperature selectivity range of that phase with respect to some pairs of isomers.

These remarks concern, of course, systems in which the liquid crystal layer is deposited on the surface of an active adsorbent. Chow and Martire[10] and Schnur and Martire[11] investigated systems in which the films of liquid crystals were deposited on the surface of non-active supports (DMCS treated) and found that the thermodynamic properties of these compounds are independent of the film thickness and that the influence of the silanized solid surface is negligible.

On the other hand, it is known that the liquid crystal molecules are arranged on the active adsorbent surface in the domains parallel to each other (along the long axes) and are at the same time oriented with respect to the adsorbent surface. Their long axes can make angles with the surface ranging from 0 to 90°. The type of orientation and the size of the angle depend on the mesophase structure and the chemical structure of the liquid crystal molecule and also on the adsorbent surface activity. The interaction of the liquid crystal molecules with the adsorbent surface is greatest in the layer directly adjacent to the surface. It is not known, however, how far (over how many successive liquid crystal molecular layers) the influence of the adsorbent surface extends, and what the properties are of the liquid crystal whose structure is under the strong influence of the surface.

The work described here was aimed at the at least partial elucidation of this problem.

EXPERIMENTAL

The properties of liquid crystal films on the solid surface were analysed on the basis of the retention volume, V_S, of n-octane and toluene, defined as

$$V_S = \frac{1}{M} \cdot j \cdot D_z \cdot \frac{d_r - d_m}{u} \cdot \frac{273.2}{T_{fl}} \cdot \frac{p_a - p}{p_a}$$

where

M = weight of adsorbent (support) in the column;
j = James–Martin coefficient;
D_z = carrier gas flow-rate at the flow meter temperature;
d_r = displacement of the maximum peak of the tested substance from the starting point as measured on the chromatogram;
d_m = displacement of the maximum peak of air;
u = chart recorder paper speed;
T_{fl} = temperature of carrier gas in bubble flow meter;
p_a = atmospheric pressure; and
p = saturated water vapour pressure at temperature T_{fl}.

The retention volume V_S was selected in view of the fact that very small amounts of the stationary phase were used in the measurements considered[12].

Johns-Manville Chromosorb P NAW with a specific surface area of 3.9 m²/g,

as measured by the method described by Serpinet[12], and particle size 60–80 mesh was used as the stationary phase support.

The stationary phase was p-butyl-p'-hexanoylazobenzene. It was found by the thermo-optical method that the transition of this compound to the nematic phase takes place at 331.7°K and the isotropic liquid region begins at 338.2°K. Further, an additional solid-phase transition is observed in the temperature range 328.2–331.7°K.

The test substances used as a "molecular probe"[13] in chromatographic measurements were analytical-reagent grade n-octane and toluene produced by Reakhim, U.S.S.R.

The retention volume measurements were made on a Chromatron chromatograph using glass columns 1 m long and 4 mm I.D. The accuracy of the temperature control with this instrument was 0.1°K in the temperature range used. Hydrogen was used as the carrier gas at a flow-rate of 40 cm³/min.

RESULTS AND DISCUSSION

Figs. 1 and 2 show $V_S = f(\tau)$ plots, where τ is the mass ratio of stationary phase to support, for n-octane and toluene, respectively. These relationships have been plotted for three temperatures at which the liquid crystal is in the solid (318.5°K), meso- (336.2°K) and isotropic liquid (359.7°K) phases. From the plots it follows that the first portion of liquid crystal (up to about 0.3–0.5%) blocks the active centres of the Chromosorb surface, which leads to a decrease in the V_S value. From a certain value of τ an increase in the retention volume is observed for both test substances, which can be explained as regards the two higher temperatures by the dissolution of these substances in the liquid stationary phase. This explanation cannot be related to the situation when the stationary phase is in the solid state, because then for n-octane V_S is in principle independent of τ, whereas for toluene the considerable increase in V_S with increasing τ is probably due to the interactions between its aromatic ring and the liquid crystal molecules lying on the surface of the adsorbent.
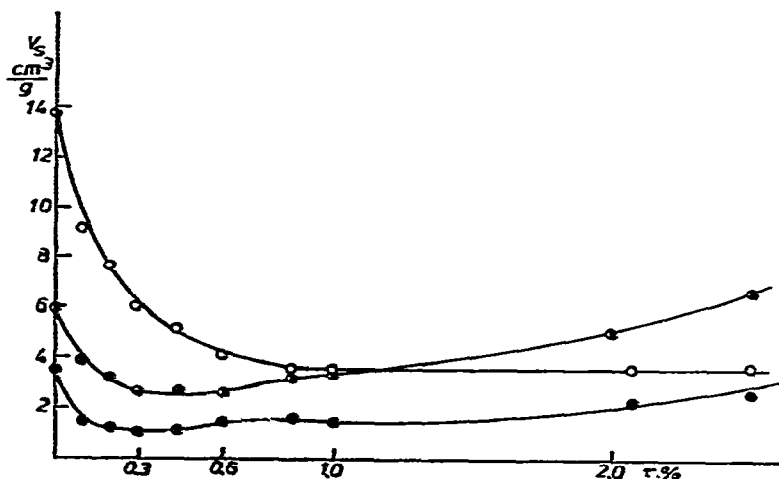

Fig. 1. $V_S = f(\tau)$ plot for n-octane at: O, 318,5 °K; ◑, 336.2 °K; and ●, 359.7 °K.
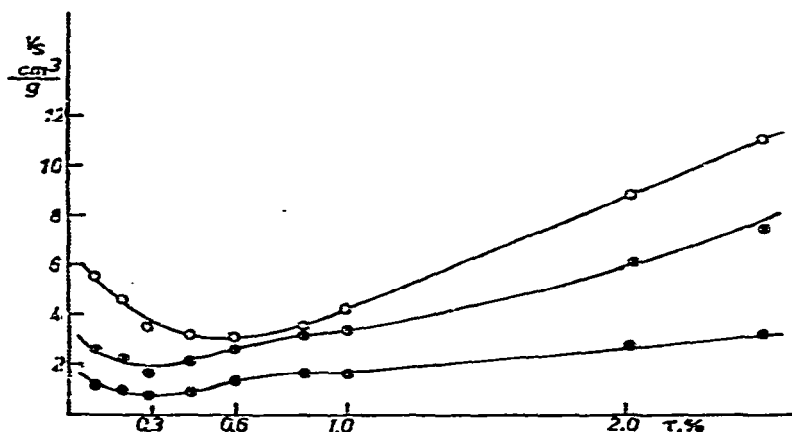
Fig. 2. $V_s = f(\tau)$ plot for toluene at: O, 318.5 °K; ◑, 336.2 °K; and ●, 359.7 °K.

These plots allow us to conclude that the retention mechanism of the chromatographed sub ances changes with the value of τ. This phenomenon is directly related to the effect of the support surface on the liquid crystal layer covering it. The range of these influences were found from the $V_s/\tau = f(1/\tau)$ plots[14]. Such plots, consisting of two intersecting straight lines, are shown in Fig. 3. The value τ_c at the intersection corresponds to the amount of the stationary phase above which no influence of the support surface is observed.

Assuming that the diameter of the p-butyl-p'-hexanoylazobenzene molecule is 0.315 nm (this value was calculated from the density and molar volume of azobenzene in the solid phase under the assumption that the density is equal to that of the liquid
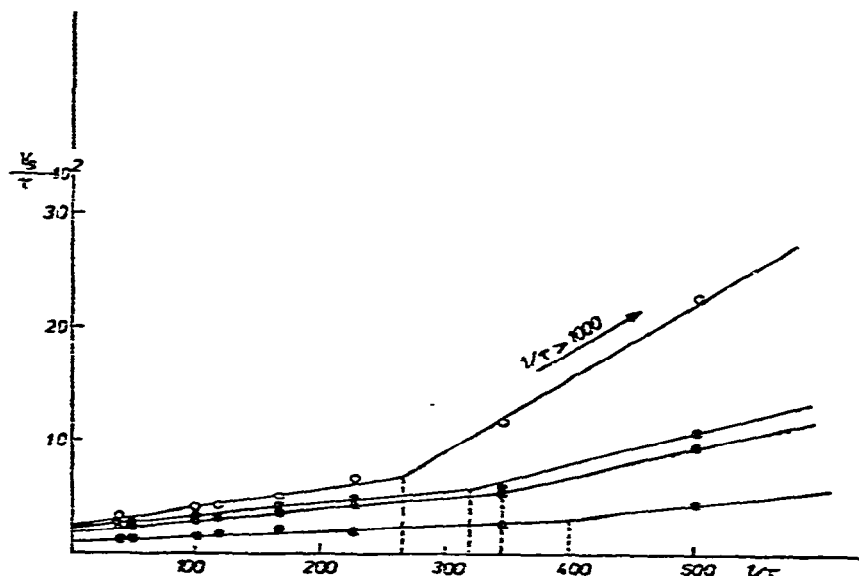

Fig. 3. $V_s/\tau = f(1/\tau)$ plot for toluene at: O, 318.2 °K; ◑, 336.2 °K; ◓, 340.2 °K; ●, 359.7 °K.

crystal and does not vary with temperature[15]), the number of molecular layers of the liquid crystal which correspond to the τ_c values at the particular temperatures were calculated from the $V_S/\tau = f(1/\tau)$ plots for n-octane and toluene.

The data in Table I indicate that the number of layers adsorbed above which the influence of the support is no longer observed depends on the temperature (or state of the liquid crystal). This can be explained by the destruction of the ordered structure of the liquid crystal molecules on the adsorbent surface with increasing temperature. The considerable differences in the numbers of layers determined for n-octane and toluene at 318.5°K are probably due to the low accuracy of determination of τ_c at that temperature caused by the short retention times.

TABLE I

VALUES OF τ_c AND THE CORRESPONDING NUMBERS OF ADSORBED LIQUID CRYSTAL MOLECULAR LAYERS

Liquid crystal state	Temperature (°K)	τ_c		Number of layers	
		n-Octane	Toluene	n-Octane	Toluene
Solid	318.5	0.0058	0.0038	3.92	2.57
Mesophase	336.2	0.0032	0.0031	2.2	2.0
Isotropic liquid	340.2	0.0029	0.0029	1.96	1.96
Isotropic liquid	359.7	0.0025	0.0025	1.69	1.69

A further question is how the layers of the liquid crystals which are under the influence of the adsorbent surface are affected in comparison with the same properties in the bulk phase. For this purpose the sorption enthalpies, ΔH, of n-octane and toluene on column packings containing varying amounts of the liquid crystal at two temperatures, corresponding to the solid state (318.5°K) and isotropic liquid (359.7°K), were determined. These relationships are shown in Fig. 4. The $\Delta H = f(\tau)$ plots at 318.5°K show a distinct maximum at $\tau = 0.3\%$, which corresponds to about two molecular layers of the liquid crystal on the surface. Another much weaker maximum occurs at $\tau = 0.8-1\%$. The $\Delta H = f(\tau)$ plots at 359.7°K have a similar shape, but the extremes of this function have lower relative values. It should be noted that a small maximum at the same coverage also occurs on the $V_S = f(\tau)$ curves at 359.7°K (Figs. 1 and 2).

The difference between the shapes of the $\Delta H = f(\tau)$ curves determined at different temperatures can perhaps be explained by the differences in the kinetic energy of the molecules in the adsorbed layer.

The above data do not allow a full interpretation of the structure of the liquid crystal layer on the adsorbent surface. Nevertheless, they support the concept that the adsorption forces on that surface "organize" the surface film in such a way that it has different properties to the liquid crystal beyond the range of these forces. This conclusion is confirmed by the shape of plots of relative retention volume ($V_S^{octane}/V_S^{toluene}$) against τ plot (Fig. 5). It can be seen that at all three temperatures a selectivity maximum occurs at $\tau = 0.3\%$ and, only at temperatures corresponding to the liquid crystal solid state and mesophase, also at $\tau = 0.8\%$. The lack of a maximum for the isotropic liquid at this coverage means that the interaction of the liquid crystal with n-octane and toluene molecules does not change in this state. The different selectivities
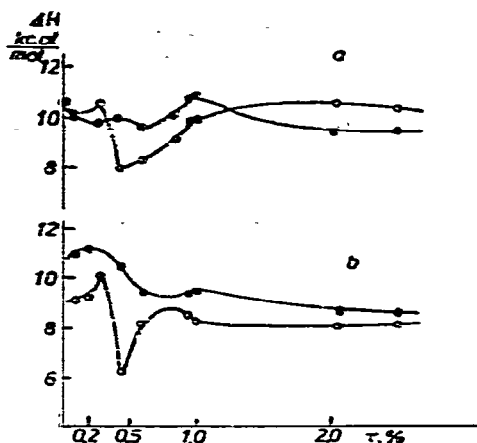
Fig. 4. Variation of (a) n-octane and (b) toluene ΔH sorption with τ at :O, 318.5 °K; and ●, 359.7 °K.

of the column packings, on which the phenomenon of dissolution of the chromato-graphed substances occurs only to a small extent, are probably due to the different surface structures of these packings, i.e., to the different structure of the liquid crystal layer. These differences are so large that they lead to a change in the elution order of n-octane and toluene.
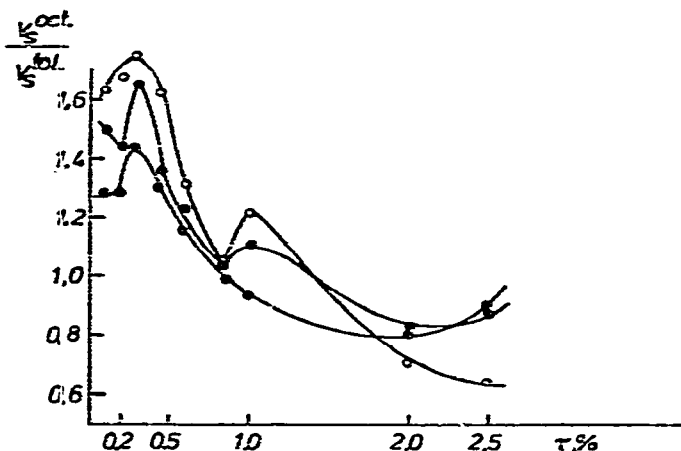

Fig. 5. Variation of the relative retention volumes ($V_S^{octane}/V_S^{octane}$) with τ at: O, 318.5 °K; ◐, 336.2 °K; and ●, 359.7 °K.

CONCLUSIONS

The effect of adsorption forces on the surface of Chromosorb P NAW on the structure of the liquid crystal film has a range of about 2 nm and corresponds to 5–6 layers of horizontally lying liquid crystal molecules. Within this range we can distinguish the following regions in which the liquid crystal has different properties:

(i) $0\% < \tau \leqslant 0.3\%$: structure characterized (at $= 0.3\%$) by a sorption ΔH maxima and selectivity maxima for n-octane and toluene;

(ii) $0.3\% < \tau \leqslant 0.8{-}1\%$: sorption ΔH minima and selectivity minima; and

(iii) $\tau > 1\%$: no "organizing" effect of the adsorbent surface on the adjacent liquid crystal film.

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