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EFFECT OF THE AMOUNT OF LIQUID CRYSTAL AND TYPE OF SUPPORT ON SOME PROPERTIES OF THE LIQUID CRYSTALLINE STATIONARY PHASE–SUPPORT SYSTEM

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SUMMARY

The effects of the amount of liquid crystalline stationary phase (from about 0.2 to about 10%) and of the type of the support on the properties of the system being formed were studied. Chromosorb P NAW, P AW, P AW DMCS and G AW DMCS were used as supports. The dependences of V_g, V_s, k' and HETP on the temperature of the column and the amount of the stationary phase on the support were studied and it was found that the interaction of the Chromosorb with the stationary phase decreases in the order NAW > AW > AW DMCS.

INTRODUCTION

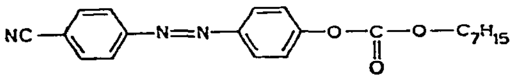
Liquid crystalline stationary phases are finding increasing application in gas chromatography[1–3]. However, they are also very suitable materials for studying support–stationary phase interactions[4–7] and for investigating the properties of thin films on supports[8–10]. Observations of the properties and behavior of liquid crystal thin films on chromatographic supports may provide information that will be useful for acquiring a knowledge of their properties when deposited on other substrates, *e.g.*, glass. In addition, the known orienting effect of the substrate on liquid crystal molecules[11–12] allows us to draw conclusions about their arrangement on the support.

In this work we have tested the effect of coverage of the support with the liquid crystal on the properties of the liquid crystal–support system and the dependence on the physico-chemical properties of the support.

EXPERIMENTAL

Column packings

The liquid crystal



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was used. The phase transition temperatures of this compound, as determined by the thermo-optical method with the Boetius heated-stage and PHMK 05 observation device, are: K 81 S 82.5 N 102.5 I. Phase transitions at 83.5 and 98°C were detected by means of a differential scanning calorimeter.

Chromosorb P (Johns-Manville, Denver, CO, U.S.A.) in three surface treatment modifications (NAW, AW and AW DMCS) and Chromosorb G AW DMCS were used as supports. The specific surface areas of the supports were determined by gas chromatography, by comparison with substances of known specific surface area using nitrogen[13]. The following values were obtained: Chromosorb P NAW 9.8 m^2/g, Chromosorb P AW 9.4 m^2/g, Chromosorb P AW DMCS 5.5 m^2/g and Chromosorb G AW DMCS 3.0 m^2/g.

Fractions of the supports of grain size 0.15–0.20 mm were heated for 3 h at 200°C. The liquid crystal was deposited on the support from a methylene chloride solution. The solvent was removed by mild heating under reduced pressure.

All of the columns were made of glass and had a length of 2.1 m and an I.D. of 4 mm. The part of the column placed in the injector (about 7 cm) was filled with crushed quartz of grain size 0.15–0.20 mm. The characteristics of the columns tested are given in Table I.

TABLE I

CHARACTERISTICS OF COLUMNS USED

Column No.	*Chromosorb*	*Weight of packing in column (g)*	*Amount of stationary phase on support (%)*	*Amount of stationary phase on surface of support* (g/m^2)
1	P AW	11.94	1.06	0.0135
2	P AW	12.72	2.09	0.0283
3	P AW	11.81	4.97	0.0624
4	P AW	12.24	9.43	0.1228
5	P AW DMCS	13.32	1.02	0.0245
6	P AW DMCS	11.01	2.19	0.0438
7	P AW DMCS	11.03	4.98	0.0999
8	P AW DMCS	13.59	9.46	0.2337
9	P AW	11.75	0.21	0.0026
10	P AW	11.99	0.59	0.0075
11	P AW DMCS	11.78	0.22	0.0047
12	P AW DMCS	11.98	0.62	0.0135
13	P NAW	11.46	0.62	0.0072
14	P NAW	10.56	1.04	0.0112
15	P NAW	11.57	2.09	0.0247
16	P NAW	10.795	5.08	0.0560
17	G AW DMCS	16.29	4.96	0.2693
18	P AW DMCS	12.92	0.42	0.0099
19	P AW	12.22	0.41	0.0053

The amount of the liquid crystal on the support was determined by calcining samples of the filling at 600°C. Table I gives the average values for three weighed portions.

Procedure

A Pye Unicam GCV gas chromatograph provided with a flame-ionization detector was used, with nitrogen as the carrier gas. The temperatures of the detector and injector were 180 and 240°C, respectively. The column packing was initially heated for 3 h at 135°C. After cooling to ambient temperature, however, not earlier than the next day, the retention times of xylene isomers at different column temperatures were measured. The xylenes were injected on to the column in the form of solutions in cyclohexane (1:50) in an amount of 0.2 μl using a 1-μl Hamilton syringe.

Testing was carried out in the temperature range 60°–120°C at 5°C intervals, and in the phase transition regions at 1°C intervals. The retention times were measured with a stop watch. Methane was used for determining the dead retention time. The carrier gas flow was measured with a soap flowmeter.

Calculations

The variation of the fundamental retention quantities specific retention volume (V_g), retention volume (V_s) and capacity ratio were investigated.

The calculations were performed with an HP 9830A calculator and plots were obtained using an automatic numerically controlled plotter.

V_g was calculated in the usual manner[14].

V_s was calculated in a similar way, taking into account the weight of the support instead of the weight of the stationary phase[15]. The capacity ratio was found

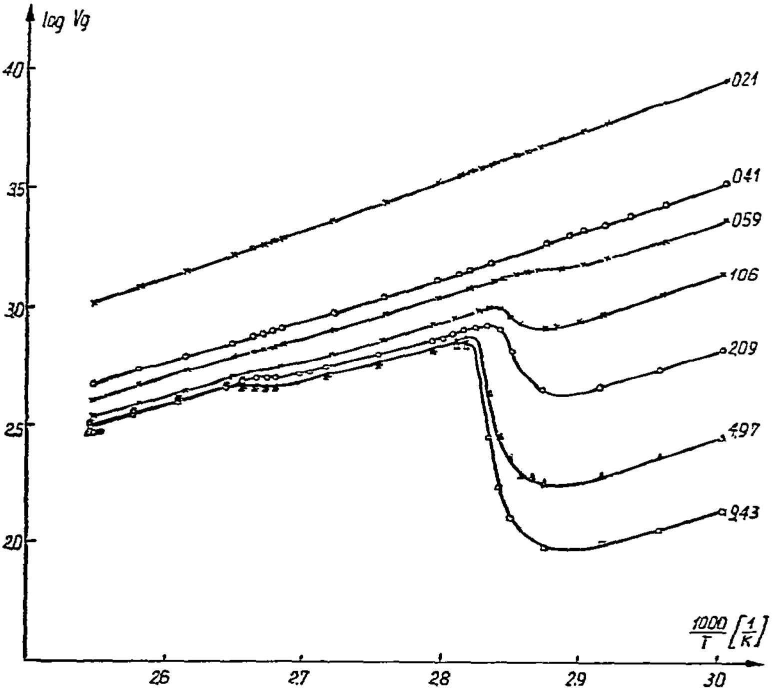


Fig. 1. Variation of the retention volume with temperature of the column for various coverages of Chromosorb P AW with the stationary phase.

from the relationship $k' = (t_R - t_d)/t_d$, where t_R is the uncorrected retention time and t_d is the dead retention time.

RESULTS AND DISCUSSION

Most of the results presented were obtained with *o*-xylene as the test substance.

In Fig. 1 the variation of the specific retention volume of *o*-xylene with temperature, log $V = f(1000/T)$, is plotted for packings with different amounts of the liquid crystal on Chromosorb P AW. Distinct differences in the course of the relationship are observed from about 1% of the liquid crystal on the support.

The changes in retention increase with increasing amount of the liquid crystal on the support. The observed relationships indicate that from about 0.6% of liquid crystal on Chromosorb P AW there are regions where the liquid crystal occurs in bulk form and the liquid crystalline structure can be generated there.

For Chromosorb P NAW it was found that the effect of the support is greater. Distinct phase transitions were observed only at about 2% of the stationary phase on the support (Fig. 2). The amount of the stationary phase per unit surface area of the support at which distinct phase transitions occur is twice as large for Chromosorb P NAW as for Chromosorb P AW.

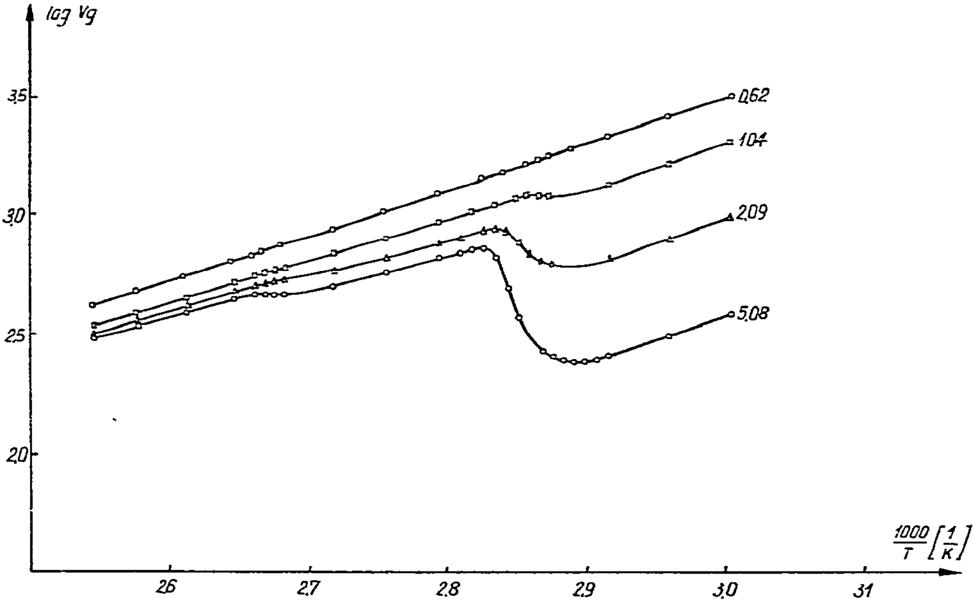


Fig. 2. Variation of the retention volume with column temperature for various coverages of Chromosorb P NAW with stationary phase.

In Fig. 3 the variation of the retention volume per unit weight of the column filling is shown for columns with Chromosorb P AW as the support. The plots indicate that the variation of the retention volume is related to the surface area of the support in situations where sorption plays a significant role, for instance in the solid-state temperature region of the stationary phase. In that region V_s decreases as the amount

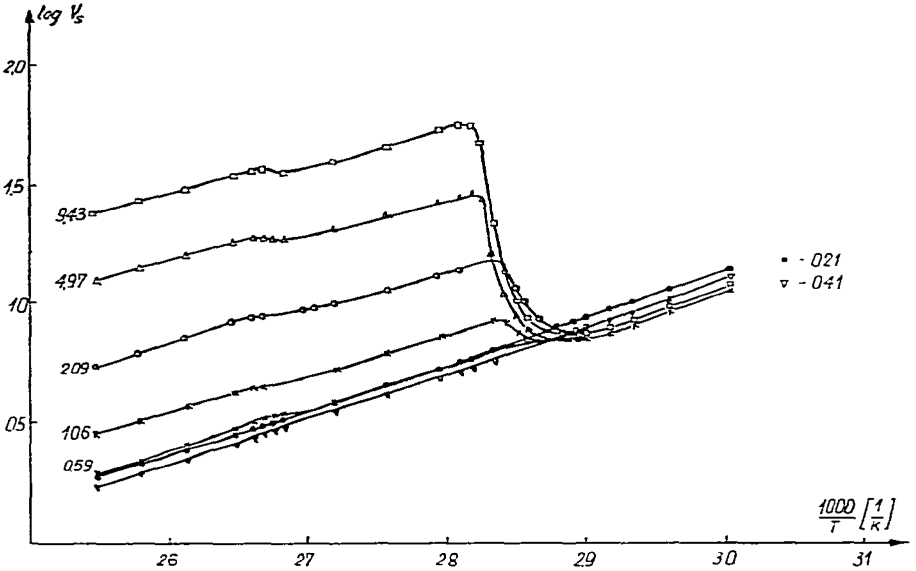


Fig. 3. Variation of V_s with column temperature for different coverages of Chromosorb P AW with the stationary phase.

of the stationary phase on the support increases from 0.21 to 0.59%. For higher coverages of the support with the stationary phase, V_s remains almost constant. Such a variation of V_s in the solid-state temperature range of the stationary phase indicates considerable sorption of the chromatographed substance on the surface of the support not covered with the stationary phase; 0.59% of the stationary phase is a sufficient amount to cover the most active sorption centres. A similar relationship was obtained for Chromosorb P NAW. For both Chromosorbs the relationship changes drastically when the melting point of the stationary phase is exceeded.

In the mesophase and isotropic liquid, dissolution begins to play a significant role in the chromatographic process, which is accompanied by an increase in V_s with increasing amount of the stationary phase.

The maxima on the $V_s = f(1000/T)$ and $V_g = f(1000/T)$ plots are usually obtained in the vicinity of the melting point of the stationary phase. It was found that only for large amounts of the liquid crystal (above 5%) does the maximum on the plots (Figs. 1 and 2) coincide with the melting point of the liquid crystal as determined thermo-optically. As the amount of the stationary phase decreases, the maximum of the plot is shifted towards lower temperatures. Figs. 4 and 5 enable us to follow these changes. In Fig. 4 the variation of the melting point is shown for columns with Chromosorb P AW as the support. The same results were obtained, however, when Chromosorb P NAW was used. Fig. 5 shows the variation of the melting point of the stationary phase deposited in different amounts on the silanized support (Chromosorb P AW DMCS). On comparing Figs. 4 and 5 it can be seen that the shifts of the melting points are greater for the silanized support than for the non-silanized supports. The melting point of the stationary phase deposited in an amount of 0.62% on Chromosorb P AW DMCS (Fig. 5), determined from the retention properties, is 70°C, *i.e.*,

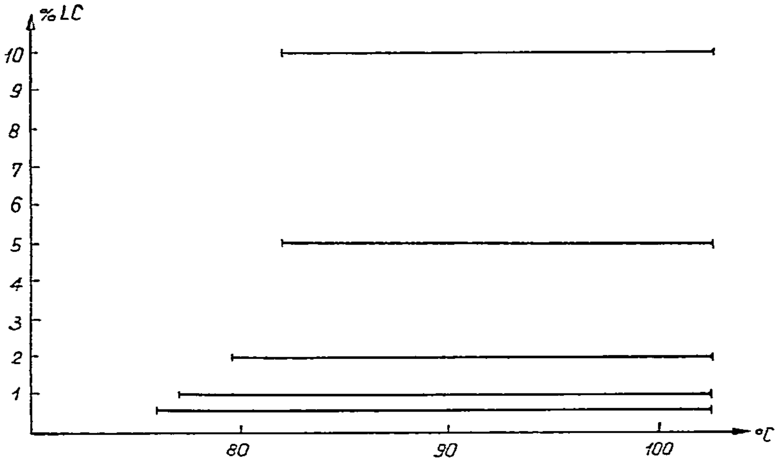


Fig. 4. Variation of the melting point with the amount of the stationary phase on Chromosorb P AW.

12°C lower than that determined thermo-optically. This difference was smaller for columns packed with Chromosorb P AW and P NAW, and did not exceed about 6°C. Above 5% of the stationary phase on all of the supports tested, the maximum of the $\log V_g = f(1000/T)$ plot fairly accurately coincides with the melting point of the liquid crystal. The dashed line in Fig. 5 shows the presence of a second stepwise increase in the retention volume. When testing column 7, containing 4.98% of the liquid crystal on Chromosorb P AW DMCS, it was found that the retention volume of xylene isomers increases stepwise below the melting point. A similar effect was observed for silanized Chromosorb G. The $\log V_g = f(1000/T)$ plots for columns packed with the silanized supports are shown in Fig. 6, where the relationship for

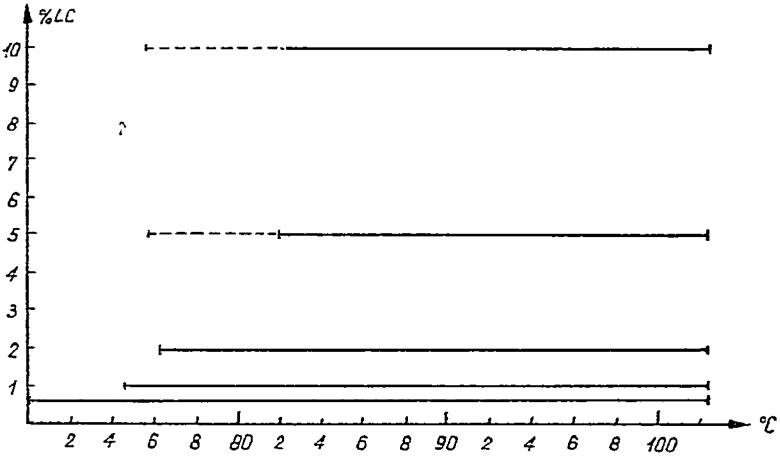


Fig. 5. Variation of the melting point with the amount of the stationary phase on Chromosorb P AW DMCS. The dashed line represents the stepwise increase of the retention properties at temperatures below the melting point.

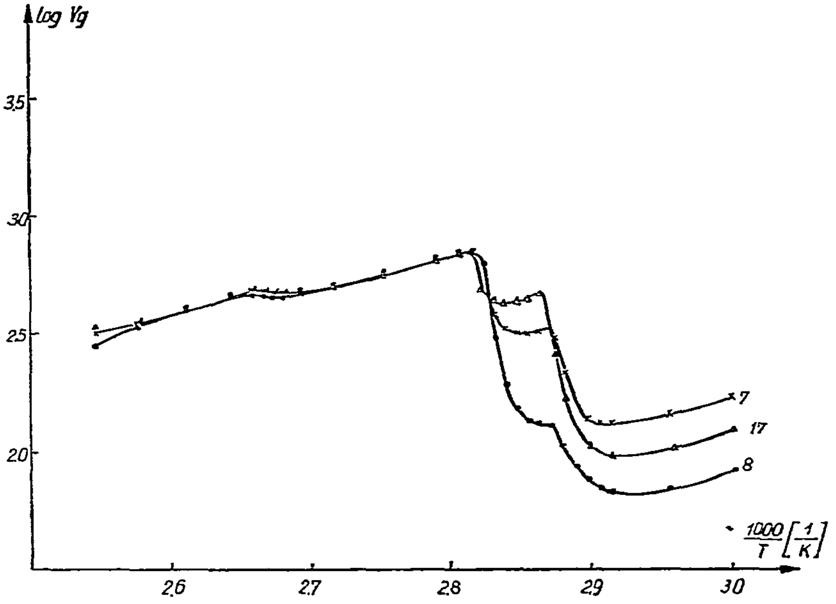


Fig. 6. Variation of the retention volume with column temperature for columns 7, 8 and 17 (Table I).

column 8, containing 9.46% of the liquid crystal on Chromosorb P AW DMCS, is also presented. The results of calorimetric investigations show that the observed increase in the retention properties is not related to a transformation in the solid, which sometimes occurs in the liquid crystals. It seems, therefore, that the effect is probably connected with the phenomena taking place at the interfaces. Transformations accompanied by step changes of the retention properties were observed by Serpinet[15–18] when studying various stationary phase–support systems. He usually used higher aliphatic alcohols as the stationary phase and Chromosorb P was one of the supports used. Serpinet explained the observed effects by the occurrence of a monolayer of the stationary phase on the surface of the support. The monolayer undergoes some phase transitions at a temperature different to that of the liquid accumulated in the pores of the support. We should note, however, that there are significant differences between the courses of the phenomena observed by Serpinet and those occurring in our tests. Those differences are as follows:

(1) All the additional transitions related to surface phenomena occur in Serpinet's studies at temperatures higher than the melting point of the stationary phase, *i.e.*, the converse of that in the systems tested here.

(2) Serpinet observed the described phenomena on many supports, but not with silanized supports, which he explained by the lack of wettability of those supports by the stationary phases tested. In the systems tested here the additional step changes of the retention properties occurred only on the silanized supports.

(3) Serpinet did not observe a strong dependence of the phase transitions on the amount of the stationary phase, in contrast to the results shown here in Figs. 4 and 5.

The above differences indicate that the phenomena observed by Serpinet do not have the same causes, despite some similiarities. However, further studies are required in order to explain whether the effects observed here are caused by the formation of a condensed monolayer, capillary effects or some other phenomena.

Figs. 7 and 8 show the variation of the retention volume, V_s, with the amount of the liquid crystal deposited on Chromosorb P AW DMCS for xylene at different temperatures. The plot obtained for Chromosorb G DMCS is similar. Distinct differences are visible in the plots of the relationship shown in Figs. 7 and 8 depending on whether the support surface was silanized or not.

The greatest difference is observed at 76°C. For Chromosorb P AW the retention volume is constant at that temperature (Fig. 7), whereas for Chromosorb P AW DMCS there is an increase in V_s as the amount of the stationary phase on the support increases to about 2%, and only then does it stabilize. For Chromosorb P AW the values of V_s at 76°C are lower over the whole range of coverages studied than those obtained at 60°C. For Chromosorb P AW DMCS, however, lower values of V_s occur only at coverages below 0.5%.

At temperatures corresponding to the solid state of the stationary phase the changes in V_s are small. For Chromosorb P AW there is a slight decrease and for Chromosorb P AW DMCS a slight increase in V_s with increasing amount of stationary phase on the support. At the melting point of the stationary phase (82°C) and at the temperatures corresponding to the isotropic liquid (102 and 110°C) the dependence

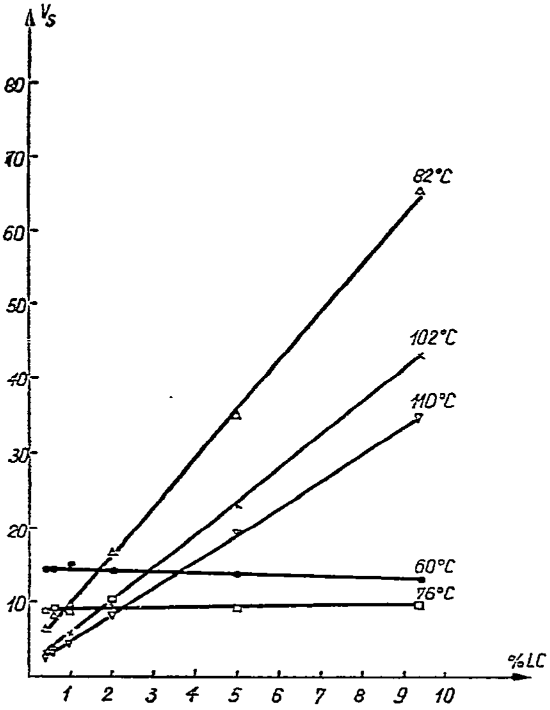


Fig. 7. Variation of the retention volume, V_s, with the amount of the liquid crystal on Chromosorb P AW.

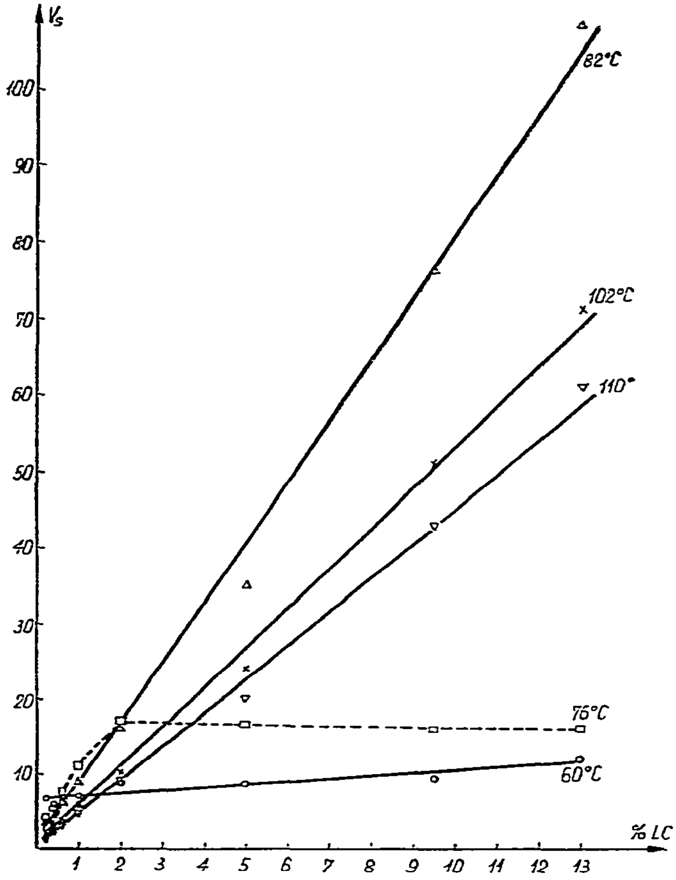
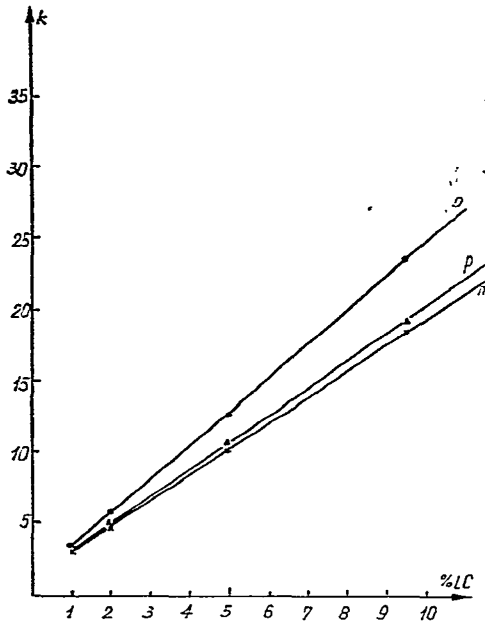


Fig. 8. Variation of the retention volume, V_s, with the amount of the liquid crystal on Chromosorb P AW DMCS.

of V_s on the amount of the stationary phase on the support is linear for both supports. With the silanized support the line is steeper, indicating a more rapid increase of V_s with increasing coverage of the support. This shows that for equal amounts of the stationary phase on the support, more of it participates in the solute dissolution process when the silanized Chromosorb is used. Also, with increasing coverage of the support by the stationary phase, the difference between the amounts of the stationary phase remaining on the surface of the support and in its pores increases. With Chromosorb W AW a considerable proportion of the stationary phase is in the pores, which are so deep that they cannot be fully penetrated by the molecules of the solute.

A quantity often used for comparative assessment of chromatographic columns and characterizing the packings is the capacity ratio, k'. In order to make such a comparison we calculated the capacity ratio for xylene isomers using the liquid crystal–support systems studied. The maximum capacity ratio occurs at the same temperature at which the maximum retention volume is observed.

Figs. 9 and 10 show the dependence of the maximum of the capacity ratio on the amount of the liquid crystalline stationary phase for the columns in which Chromosorb P AW (Fig. 9) and Chromosorb P AW DMCS (Fig. 10) are used as supports. With the former support the maximum values of the capacity ratio increase linearly with the amount of stationary phase deposited. With the silanized support the capacity ratio shows a steeper, non-linear growth. For the same amount of the stationary phase the values of the capacity ratio are greater for the silanized than for the non-silanized support. When the stationary phase is deposited on the silanized support the differences in the separation ratios for the particular xylene isomers are greater.



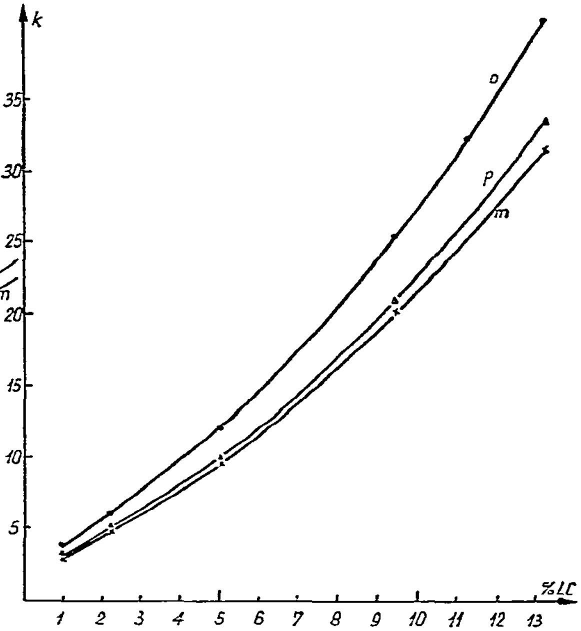


Fig. 9. Dependence of the capacity ratio for xylene isomers on the amount of the stationary phase on Chromosorb P AW.

Fig. 10. Dependence of the capacity ratio for xylene isomers on the amount of the stationary phase on Chromosorb P AW DMCS.

The tests have shown that there is a strong dependence of the properties of the liquid crystal–support system on the amount of the liquid crystal deposited on the support and on the physico-chemical character of the support surface. Liquid crystals, in view of their properties and ordered structure, are more sensitive to the effect of the substrate than are conventional stationary phases. The effect of the support surface on the liquid crystal molecules for Chromosorb P decreases in the order NAW > AW > AW DMCS. The differences in the properties of the liquid crystalline stationary phase related to the type of support surface are due to the different interactions of the polar molecules of the stationary phase with the support. This interaction is greatest and involves the largest number of molecules with Chromosorb P NAW and is smallest, involving the least molecules, with Chromosorb P AW DMCS. However, in order to be able to predict the properties of different liquid crystal–support systems and to select systems that would have the best properties from an analytical point of view we require a better knowledge of the liquid crystal–support interactions.

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