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The Adsorption - Absorption Gas Chromatography on Silochromes with Layers of Liquid Crystals

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The results of studies of the properties of liquid crystals in a version of gas adsorption-absorption chromatography are surveyed. A general property of liquid crystals deposited on active adsorbent carriers, consisting in the possibility of extending the temperature range of the existence of their mesomorphic state, is revealed.
The bibliography includes 94 references.

CONTENTS

I. Introduction 879
II. The influence of various factors on the structural selectivity of thermotropic liquid crystals 880
III. The phase transitions in the mesomorphic state of a smectic liquid crystal 883
IV. Assessment of liquid crystal stationary phases on the basis of polarity factors 884

I. INTRODUCTION

Liquid crystals (LC) possess simultaneously the properties of liquids (fluidity, the ability to exist in the form of drops, etc.) and the properties of solid crystalline bodies (anisotropy, and electrical, optical, and other properties)[1]. Friedel[2] was the first to introduce the concept of the mesomorphic (liquid crystal) state and divided liquid crystals into two types: nematic and smectic. Certain liquid crystals belong to both types. In this case the smectic mesophase, in which molecules are not only arranged parallel to one another but are also fixed in layers, is formed initially; at higher temperatures there is a transition to the nematic mesophase, where this additional order is lost. A further increase of temperature leads to the formation of the isotropic liquid. The formation of a special kind of "twisted structure" is characteristic of the cholesteric mesophase, which is regarded as a variety of the nematic phase[1].

Liquid crystals can be formed not only on fusion of a solid (thermotropic liquid crystals) but also in the course of its dissolution (lyotropic liquid crystals). The chemical features, structure, and properties of low-molecular-weight liquid crystals have been described in reviews[3-5] and in a monograph[6].

The liquid crystal state is characteristic not only of many low-molecular-weight compounds but also of high-molecular-weight compounds. As early as 1941, Kargin and Slonimskii[7] and later Sanderman and Keller[8] drew attention to the possibility of the existence of the liquid crystal state in polymeric systems. However, theoretical and experimental studies only recently established that the phase transition of polymers to the mesomorphic state is just as feasible as for low-molecular-weight compounds.

The formation of liquid crystal polymers induced by the entropy effect as a result of the rigidity of the main chain has been described in a review[9]. Liquid crystal systems in which the ordering of the side groups is possible by virtue of the flexibility and not rigidity of the main chain have been examined, for example, in Refs.10–13. Plate et al.[14] proposed a new approach to the formation of liquid crystals of the thermotropic type from high-molecular-weight, which consists in synthesising mushroom-shaped polymers containing mesogenic groups at the ends of the side branches. The mesomorphic state of liquid crystals possesses a unique combination of properties, which is responsible for their wide scale employment in optics, holography, quantum electronics, visual observations of temperature changes by only 0.01–0.001 K, and the elucidation of molecular structures by NMR spectroscopy, as structural elements in living organisms, and finally as specific sorbents in the chromatographic separation of isomeric compounds. The applications of liquid crystals have been reviewed fairly completely[15].

On the other hand, the first studies of the chromatographic characteristics of liquid crystals demonstrated their likely usefulness as sorbents for gas chromatography[16-19]. The ordered arrangement of molecules in the temperature range of the mesophase promotes the separation of aromatic *meta*- and *para*-isomers with similar boiling points. This effect, first observed[16-19] for azoxy-esters, proved to be characteristic of many liquid crystals: it arises because the more linear form of the *para*-substituted aromatic compounds enables them to penetrate more readily into the liquid crystal lattice and to interact more "intimately" than the *meta*- and *ortho*-substituted derivatives. This property has been noted in a number of studies[20-27] where it was shown that the maximum selectivity of the liquid crystals with respect to positional isomers is observed at the melting point and diminishes with increase of temperature, while the sorption capacity of the chromatographic column also increases sharply on passing from solid to the mesomorphic state of the liquid crystal.

Liquid crystals have found extensive applications in gas chromatography as highly selective stationary phases. Fairly numerous publications, including reviews, have been devoted to this problem[22,23,28-30]. The possible analytical applications of many known and also newly synthesised liquid crystals have been investigated by Soviet workers[28,31-42]. Difficult separations have been achieved on liquid crystals using not only packed but also micropacked[43] and capillary columns[44-47]. Chemical modification of the silica surface with cholesteric liquid crystals makes it possible to employ such sorbents for highly effective liquid chromatography[48].

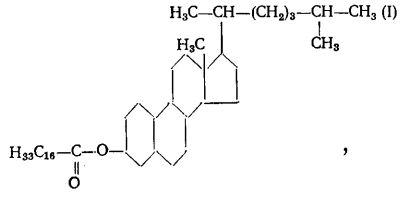
Liquid crystals have been used to separate the homologues of naphthalene[49], polynuclear aromatic hydrocarbons[50,51], steroids[52], polycyclic aromatic hydrocarbons up to C_{24}, [53] benzopyrene[54], herbicides[55], etc. A comparison has been made[56] of columns with bentonites and liquid crystals; it has been shown that the selectivity of liquid crystals with respect to *ortho*-, *meta*-, and *para*-isomers is in many instances greater. Theoretical problems concerning the selectivity of liquid crystals have been examined in a number of studies[36, 57-60].

One should note that accurate measurements, such as the determination of thermodynamic characteristics on liquid crystals[58,61-65], the determination of the orientational order in cholesteric[66] and nematic liquid crystals[67], the observation of a change in the selectivity and sorption capacity of the chromatographic column with liquid crystals following the application of an electric field[68-70], and the determination of the temperatures of transitions from one phase state of liquid crystals to another[58], can be carried out with the aid of chromatography.

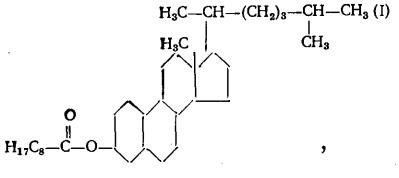
II. THE INFLUENCE OF VARIOUS FACTORS ON THE STRUCTURAL SELECTIVITY OF THERMOTROPIC LIQUID CRYSTALS

In all the studies quoted, except those of Zelenkova and coworkers[41,42], substances have been separated as a result of their dissolution in a film of liquid crystals deposited on an inert solid support, which hardly altered the properties of the liquid crystals and did not itself participate in the sorption of the components to be separated. We replaced the support with a low adsorption activity and a low specific surface ($s_{sp} \cong 1$ m^2 g^{-1}), usually employed, by a silica adsorbent support (silochrome) with $s_{sp} \cong 10$–150 m^2 g^{-1}.[71] It was assumed that, owing to the strong adsorption, there is a definite orientation of the polar molecules of the liquid crystal on the surface of the adsorbent support and that this rigidly fixed orientation persists over a wider temperature range due to the adsorption field of the adsorbent support. This made it possible, in its turn, to retain the selectivity of the liquid crystals with respect to isomers over a wide temperature range and for different amounts of liquid crystals.

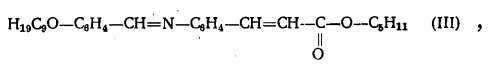
For this purpose, we used the adsorption–absorption variant of gas chromatography (GAAC),[72] which is intermediate between the gas-adsorption and gas-liquid variants and presupposes retention, as a result of both adsorption and dissolution (absorption), of the specimen in a film of liquid phase deposited on the adsorbent support. Nematic and smectic liquid crystals as well as cholesteric forms of nematic liquid crystals were investigated: cholesteryl oleate



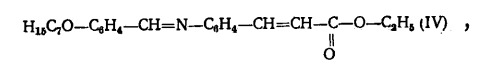
cholesteryl pelargonate



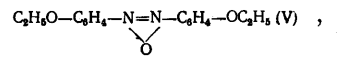
n-pentyl *p*-(n-nonyloxy)benzylidene-*p'*-aminocinnamate



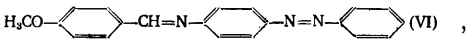
ethyl *p*-(n-heptyloxy)benzylidene-*p'*-aminocinnamate



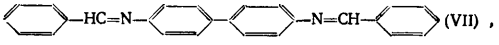
4,4'-diethoxyazoxybenzene



p-anisylideneaminoazobenzene



and *p,p'*-dibenzylidenebenzidine



The phase transition temperatures and the clarification temperatures t_{cl} of liquid crystals (I)–(VII) are listed below:

LC	(I)	(II)	(III)	(IV)	(V)	(VI)	(VII)
t, °C	19 (smc)	78 (smc)	80 (sosm)	120 (sosm)	135 (son)	147 (son)	234 (son)
t_{cl}, °C	33.5	91.5	135	156	165	183	260

(the following phase symbols are used for the specified phase transition temperatures: so = solid, sm = smectic, n = nematic, and c = cholesteric).

Specific macroporous adsorbent silochromes[73] with $s_{sp} = 120$, 150, 80, 50, 30, and 10 m^2 g^{-1}, a non-specific carbon adsorbent—PM-15 carbon black, and CaA molecular sieve ($s_{sp} \cong 800$ m^2 g^{-1}) were used as supports for the liquid crystals. The column size was 100×0.3 cm and the linear flow rate of nitrogen was 17 sm s^{-1}. For comparison, the liquid crystals were deposited also on the usual supports with a low activity: Chromaton ($s_{sp} = 1$ m^2 g^{-1}) and porous Teflon ($s_{sp} = 8$ m^2 g^{-1}).

Experimental measurements of the temperature variations to the retention volumes (V_g) on liquid crystals deposited on adsorbent supports confirmed the initial hypotheses. Fig. 1*a* presents the temperature variation of lg V_g of xylene isomers on cholesteryl pelargonate deposited on Chromaton ($s_{sp} \cong 1$ m^2 g^{-1}) in an amount of 6 wt.% (film thickness $\sigma \cong 60$ nm). Fig. 1*a* shows that the nature of these curves is consistent with the usual idea concerning the phase transition of liquid crystals when the temperature is varied, namely the plot shows clearly three regions of the phase states of cholesteryl pelargonate; solid, liquid crystal (mesophase), and liquid (isotropic region). The transition of cholesteryl pelargonate from the solid to the mesomorphic state is accompanied by a sharp increase of the V_g of the sorbates, i.e. at the melting point of 78 °C the retention times increase by a factor of ~5. In the region of the mesophase (78–91.5 °C) a further increase of temperature entails a decrease of V_g. In the transition of cholesteryl pelargonate to the isotropic liquid phase the retention parameters again increase but to a lesser extent. At the clarification point (91.5 °C) of the liquid crystal the selectivity of the separation (the factor α defined as the ratio of the corrected retention times of the *para*- and *meta*-isomers) diminishes. Whereas the values of V_g for the isomeric xylenes are similar in the region of the solid state of cholesteryl pelargonate and the isomers are not separated, in the region of the mesophase the V_g differ and the xylenes can be separated (Fig. 1*a*).

Thus the maximum selectivity of cholesteryl pelargonate with respect to the *meta*- and *para*-isomers is shown at the temperature where it undergoes a transition to the liquid crystal state and then decreases monotonically as the clarification point is approached. When the same amount of the liquid crystal (6 wt.%) is deposited on an active sorbent—Silochrome S-80 ($s_{sp} \cong 80$ m^2 g^{-1}) with a film thickness $\sigma \cong 0.7$, the nature of the phase transition curves changes markedly. Fig. 1*b* shows that in the region of temperatures corresponding to the transition of compound (II) to the mesophase no sharp and abrupt alteration of the retention parameters of the sorbates is observed. On the other hand, over the entire experimental range, an increase of temperature is seen to entail a decrease of the retention volumes. This

behaviour has also been observed[71] for monolayers of compounds (III) and (V) on Silochrome S-80.

The retention of a fairly high selectivity on such sorbents over the entire temperature range of the liquid crystal state of the given substance is of greatest interest. The initial adsorbent carrier does not separate xylene isomers and the selectivity in the separation is therefore due to the liquid crystal film. This unusual effect has been studied in detail in our investigations[71,74,75] for different ratios of the liquid crystal and the adsorbent carrier, i.e. a study was made of the influence of the thickness of the liquid crystal film on the effect of phase transitions; in addition the influence of the specific surface of the adsorbent carrier on this effect with retention of the chemical nature of the surface of the carrier was investigated in relation to both specific and non-specific adsorbents.

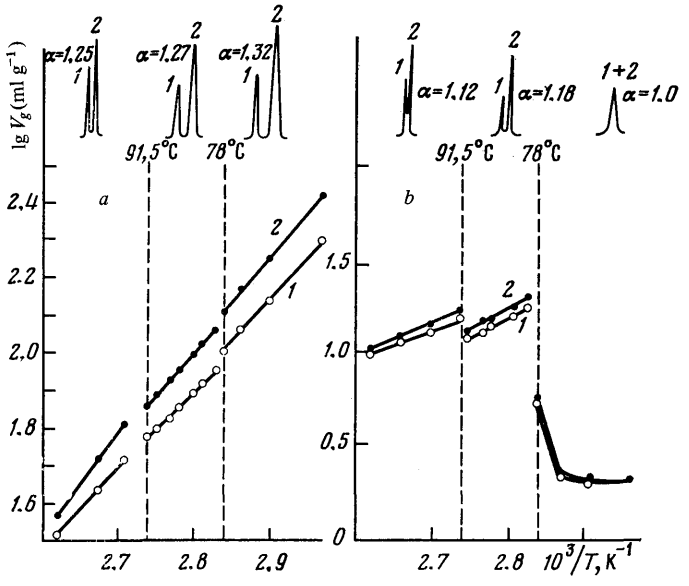


Figure 1. Temperature variation of the logarithms of the retention volumes (lg V_g) of xylene isomers on dehydroxylated Silochrome S-80 (*a*) and Chromaton (*b*) with 6 wt.% of cholesteryl pelargonate: 1) *m*-xylene; 2) *p*-xylene. The separation factors α for the pair of components at different temperatures are indicated[71].

It might have been supposed that the retention of a high selectivity obtains solely in the presence of small amounts of the liquid phase, i.e. for thin liquid crystal films, and that with increase of the film thickness on Silochrome S-80 a sharp increase of the retention parameters of the sorbates in the transition of compound (II) to the mesophase would be observed (as on a relatively inactive support—Chromaton). However, in the study of Silochrome S-80 specimens containing between 0.5 and 120 wt.% of compound (II) no breaks were observed in the relation between lg V_g and $1/T$. This can be explained by the fact that an increase of temperature does not lead to phase transitions, i.e. that the liquid crystal layers exist in the adsorbed state and that the adsorption energy exceeds the kinetic energy of the liquid crystal molecules corresponding to the given temperature.

At the liquid crystal clarification temperature there are also virtually no changes in the retention volumes.

Consequently the 6 wt.% of the liquid crystal on the surface of Silochrome S-80 has no phase transitions in the temperature range from 60° to 107 °C. The same behaviour of the liquid crystal has been observed also on Chromaton when a small amount of the liquid phase is deposited on its surface. For example, in the presence of 1 wt.% of the liquid crystal on Chromaton (Fig.2*a*) a virtually monotonic decrease of the retention characteristics with increasing column temperature is observed (by analogy with Silochrome). However, in this case the separation of xylene isomers is not observed even in the region of the mesophase.

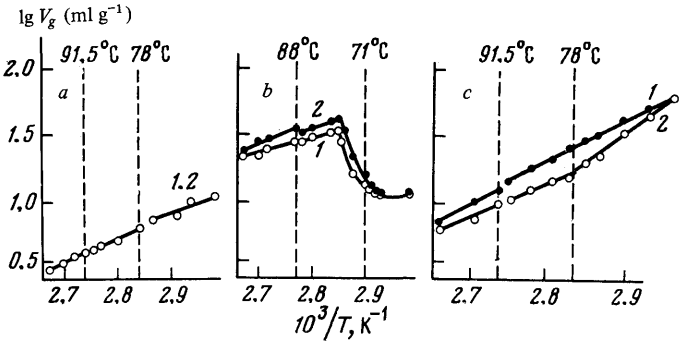


Figure 2. Temperature variation of lg V_g for xylene isomers on dehydroxylated Chromaton with 1 wt.% (*a*) and 12 wt.% (*b*) of cholesteryl pelargonate and on the same sorbent with 6 wt.% of aerosil dispersed in cholesteryl pelargonate (*c*):[74] 1) and 2) see Fig.1.

Similar relations have been observed by Gabitova and Vigdergauz[76] who noted a sharp decrease of the selectivity of the liquid crystal with respect to the *meta*- and *para*-isomers on reduction of the content of *p,p'*-ethoxymethoxyazoxybenzene on Chromosorb P to 1.2 wt.%. With increase of the content of compound (II) to 6 wt.% (Fig.1*a*) and to 12 wt.% (Fig.2*b*) on Chromaton, there is an abrupt increase of the retention characteristics on transition of the liquid crystal to the mesophase.

When the liquid crystal is deposited on Silochrome S-80 (an adsorbent with a high specific surface and a high adsorption potential), a definite orientation and ordering in the arrangement of the liquid crystal molecules on the surface of the adsorbent carrier apparently take place as a result of the adsorption field of the carrier. On further increase of the amount of liquid crystal on Silochrome, the molecules of the former are oriented relative to the liquid crystal molecules which have already been ordered. This orientation is probably close to the orientation of the molecules in the liquid crystal state and the selectivity of the separation is therefore high. As a result of the strong adsorption field of the surface of the adsorbent carrier, the ordered state persists over a wide temperature range (Fig.1*b*). Whereas the *meta*- and *para*-isomers of xylene are separated on Chromaton (Fig.1*a*) only at the melting point of compound (II), on Silochrome (Fig.1*b*) the xylenes are separated over the entire range of the specified temperatures.

Thus liquid crystals deposited in large amounts (in excess of 6 wt.%) on inert carriers with a low specific surface are selective only over a narrow temperature range, i.e. the temperature range of the anisotropic (mesomorphic) region is the only one where liquid crystals can be used. On the other hand, sorbents based on liquid crystals on an active adsorbent with a high specific surface are selective over a wide temperature range.

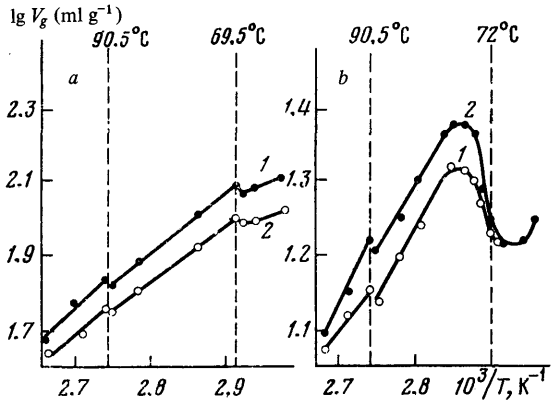


Figure 3. Temperature variation of lg V_g for xylene isomers on dehydroxylated Silochrome S-50 with 30 wt.% of cholesteryl pelargonate and on Silochrome S-10 with 6 wt.% of cholesteryl pelargonate[74]: 1) and 2) see Fig.1.

Apart from the high adsorption potential[1], the specific surface of the adsorbent support plays a major role in the attainment of a specific orientation and an ordered arrangement of the liquid crystal molecules. Fig.3 presents the temperature variation of lg V_g for xylene isomers on Silochrome with different values of s_{sp}. Thus, with decrease of s_{sp} of the Silochrome to 50 m^2 g^{-1} (Fig.3*a*) a large excess of the three-dimensional solid liquid crystal is already observed, which is indicated by the phase transition at 69.5 °C. There is also a phase transition at 90.5 °C, where the condensed film is transformed into a liquid. With decrease of s_{sp} of the Silochrome to 10 m^2 g^{-1} (Fig.3*b*), the nature of the curves representing the relation obeys the familiar hypothesis concerning the phase transitions of liquid crystals; however, the transition from the solid state to the mesophase is not so sharp as in the case of Chromaton (Fig.1*a*).

The temperature variation of the structural selectivity has been obtained[74] for liquid crystal (II) deposited on carriers with different values of s_{sp}; the maximum separation factor α is observed for compound (II) deposited on Silochrome S-150 ($s_{sp} = 153$ m^2 g^{-1}).

The influence of the chemical nature and geometrical structure of the adsorbent carrier surface on the mesomorphic state of a thermotropic liquid crystal has been investigated[74]. The temperature variation of the retention characteristics of xylene isomers was investigated on Silochromes—adsorbents of the same type but with different chemical surfaces (hydroxylated, dehydroxylated, and silanised Silochromes)—modified with cholesteryl pelargonate. On the silanised Silochrome S-180 with a liquid crystal monolayer (6 wt.%), it was observed that the xylene isomers are not separated over the entire specified temperature range (Fig.4*a*). This can be explained by the fact that the silanised (i.e. treated with hexamethyldisilazane) Silochrome is non-polar and that the adsorption of liquid crystal molecules on it is greatly reduced in contrast to the hydroxylated Silochrome; therefore, for a liquid crystal content of 6 wt.%, an ordered orientation of the liquid crystal molecules on the adsorbent surface does not take place and the xylene isomers are not separated. On the Silochrome hydroxylated to the maximum extent (continuous coverage by OH groups) with a monolayer of compound (II) (Fig.4*b*), the xylene isomers are separated just as completely as on the dehydroxylated Silochrome (OH groups removed from the surface by heat treatment at

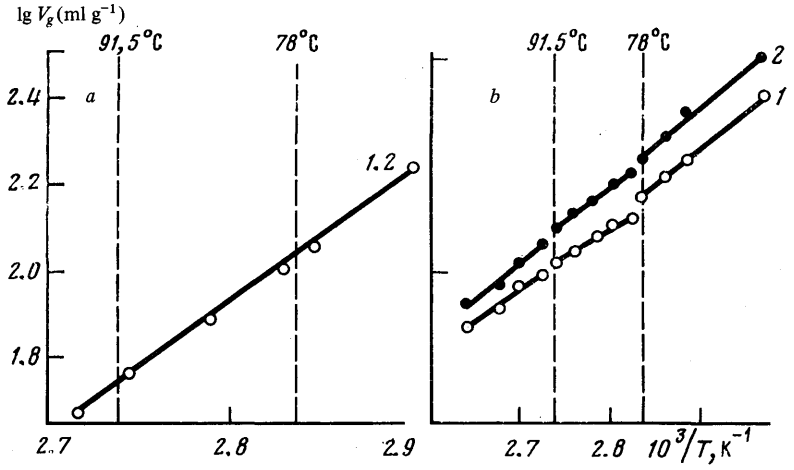


Figure 4. Temperature variation of lg V_g for xylene isomers on silanised (*a*) and hydroxylated (*b*) Silochrome S-80 with 6 wt.% (*a*) and 15 wt.% (*b*) of cholesteryl pelargonate[74]: 1) and 2) see Fig.1.

1000 °C) (Fig.1*b*). This finding confirms the hypothesis that, for the ordered parallel arrangement of the liquid crystal molecules, the nature of the surface, i.e. the nature of the adsorption forces of the adsorbent support, plays a major role.

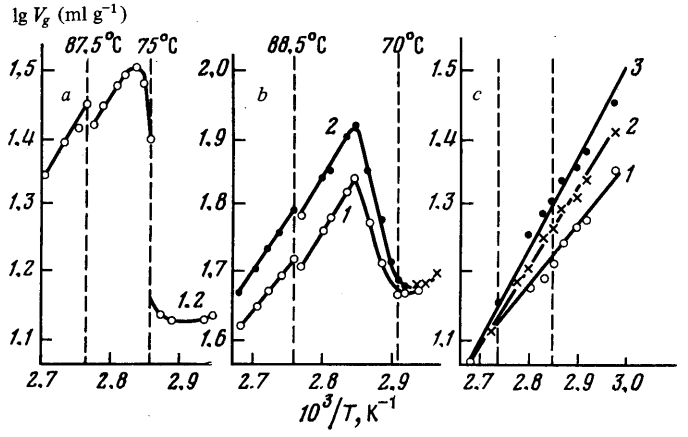


Figure 5. Temperature variation of lg V_g for xylene isomers on porous Teflon with 6 wt.% of cholesteryl pelargonate (*a*), PM-15 carbon black with 25 wt.% of cholesteryl pelargonate *b*), and CaA molecular sieve with 6 wt.% of cholesteryl pelargonate (*c*):[74] 1)–3) *m*-, *p*-, and *o*-xylenes respectively.

Fig.5 presents the temperature variation of lg V_g on carriers exhibiting marked chemical differences. Thus, on porous Teflon (a non-polar adsorbent with a weakly adsorbing surface) there is a distinct transition of the liquid crystal from the solid to the mesomorphic state, but the xylene isomers are not separated even in the region of the mesophase (Fig.5*a*). When the support is replaced by a non-specific carbon adsorbent—the PM-15 carbon black ($s_{sp} = 15$ m^2 g^{-1}), there is no sharp and abrupt change in the retention parameters (Fig.5*b*). In this case the fusion of the liquid crystal takes place gradually and not abruptly, the melting point of the liquid crystal being displaced towards lower temperatures. This can be explained by the fact that the liquid crystal film on the surface of the carbon adsorbent is acted upon by its adsorption field and the physical properties of the film therefore differ from those of the bulk-phase liquid[77]. When the CaA molecular sieve ($s_{sp} \approx 800$ m^2 g^{-1}) is used as the support for a thin film of compound (II), phase transitions at 78° and 91.5 °C are not observed and the liquid crystal exists in the form of a "condensed" film (Fig.5*c*). At 95 °C and above the liquid crystal does not exhibit selectivity with respect to the *meta*- and *para*-isomers, which apparently indicates the absence of an oriented arrangement of the liquid crystal molecules on the surface of the CaA molecular sieve. In the range 60–95 °C the selectivity of the liquid crystal decreases monotonically.

When silica (aerosil) was introduced into the liquid crystal in proportions of 1:1, i.e. on deposition of 6 wt.% of the liquid crystal and 6 wt.% of aerosil on Chromaton, appreciable phase transitions at 78° and 91.5 °C were not observed either (Fig.2*c*), and the behaviour was analogous to that observed on deposition of 30 wt.% on Silochrome S-80. However, the maximum selectivity occurs only at 78 °C (Fig.2*c*).

Thus the high structural selectivity with respect to positional isomers, the low viscosity in the region of the nematic and smectic mesomorphic states, and the high thermal stability of certain liquid crystals make it possible to recommend them for the separation of complex chemical compounds.

III. THE PHASE TRANSITIONS IN THE MESOMORPHIC STATE OF A SMECTIC LIQUID CRYSTAL

Several modifications of thermotropic smectic (soap-like) liquid crystals (SLC) can be distinguished[78]. The smectic mesophase A (S_A) consists of layers freely mobile relative to one another. The mesophase S_A is the highest-temperature phase and is least "organised" among the SLC. The smectic mesophase B (S_B) is more ordered than S_A. The smectic mesophase C (S_C) is analogous to the mesophase S_A but differs from it by the inclination of the molecular axes.

In addition to the physical methods for the investigation of liquid crystals, it is possible to employ the GAAC variant to study the phase transitions in SLC in the mesomorphic state. A study of the retention characteristics of xylene isomers on liquid crystal (III) deposited on Chromaton in an amount of 10 wt.% showed[79] that this SLC exhibits polymorphism (Fig.6*a*), namely in the region of the mesomorphic state (80–134 °C) the plot shows three breaks corresponding to the smectic states A, C, and S. As stated above, the phase states A, C, and S differ from one another by the different arrangements of the molecules in the smectic layers[78] and in this connection a triple increase of the retention parameters of the sorbate is observed.

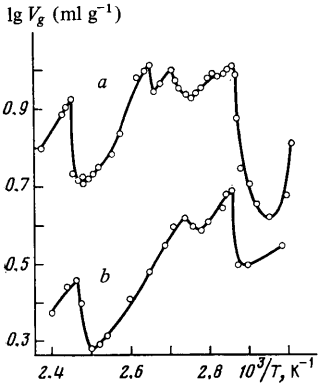


Figure 6. Temperature variation of lg V_g for *p*-xylene on dehydroxylated Chromaton with 10 wt.% (*a*) and 3 wt.% of n-pentyl *p*-(n-nonyloxy)benzylidene-*p*-aminocinnamate[79].

The polymorphism of the liquid crystal state of the test substance has been confirmed by microscopic and differential thermal (DTA) analyses. Fig.7 presents the heating and cooling thermograms for liquid crystal (III); the peak at 93 °C, corresponding to the transition from one liquid crystal modification to another, is clearly visible[79]. The peaks on the thermogram at 74° and 135 °C correspond to fusion and the transition to the isotropic liquid. It follows from the DTA that the substance has two modifications. However, microscopic analysis (Fig.8) demonstrated the presence of

three modifications. Yet another polymorphic transition occurs at 101 °C. According to Sackmann's classification[80], the test substance has smectic A, C, and S modifications which exist in the temperature ranges 135–101 °C, 101–93 °C, and 93–74 °C respectively (Fig.8). It may be that the S_A–S_C transition, which is not shown by the DTA curve of the second kind, or at any rate the thermal effect corresponding to this transition, is small.

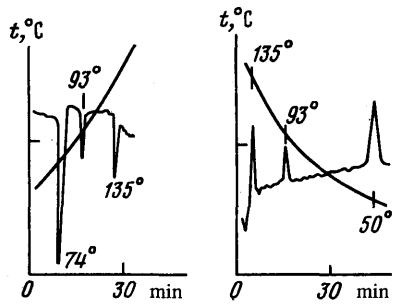


Figure 7. Heating and cooling thermograms for n-pentyl *p*-(n-nonyloxy)benzylidene-*p'*-aminocinnamate[79].

With decrease of the content of liquid crystal on Chromaton, i.e. in the case of a thin film (Fig.6*b*), the plot shows only two breaks. Fig.6*b* also shows that, with decrease of the amount of liquid crystal on the solid carrier, the phase transition temperature shifts towards lower values and the selectivity with respect to positional isomers falls. Similar features have been observed[76] in a study of the thermotropic liquid crystal *p*-methoxyethoxyazoxybenzene.

IV. ASSESSMENT OF LIQUID CRYSTAL STATIONARY PHASES ON THE BASIS OF POLARITY FACTORS

The existing methods for the estimation of the polarities of stationary phases have been examined in fair detail in a number of reviews[81–83]. Among all the known methods, the procedure proposed by Rohrschneider[84] and improved by McReynolds[85] has received the greatest recognition. It was of interest to assess the liquid crystals investigated in terms of selective properties as stationary phases (SP) with unique chromatographic properties.

We attempted[86] to classify such variable-selectivity sorbents by analogy with the methods used in gas–liquid chromatography. The possibility of using Brown's method[87] and the system of Rohrschneider's polarity factors[88] was tested on the basis of experimental results. According to Rohrschneider[88], the difference between the Kovats indices[89] on the test and standard stationary phase is a measure of the polarity of the stationary phase.

We determined the polarities of sorbents based on Silochromes and liquid crystals as the differences between the Kovats indices on squalane and the test sorbent:

$$\Delta I = I_{test} - I_{sq} \quad .$$

The overall quantity

$$\sum \Delta I = ax + by + cz + du + es \qquad (1)$$

characterises the polarity of the stationary phase and the components of the sum represent the degree of interaction of each reference substance (benzene, ethanol, ethyl methyl ketone, nitromethane, and pyridine) with the stationary phase. The polarity coefficients of the substances analysed (*a*, *b*, *c*, *d*, and *e*) must remain constant on different stationary phases[90]. In estimating the selectivity of stationary phases for the separation of positional isomers, Vigdergauz et al.[91] introduced and additional term into Eqn.(1), characterising the selectivity of the mesophase with respect to the *meta*- and *para*-isomers.

The polarity factors for different phase states of the following liquid crystals have been determined[86] by Eqn.(1): (II), (V), and (III). The results are in Table 1. For comparison, the table also includes the polarity factors for the adsorbent supports.



Figure 8. Textures of the liquid crystal state of n-pentyl *p*-(n-nonyloxy)benzylidene-*p'*-aminocinnamate[79].

As already mentioned, the nature of the curves for the temperature variation of V_g of several isomers of organic compounds is inconsistent with the classical concept of the phase transitions in liquid crystals as a function of temperature, namely that the retention characteristics diminish with increasing column temperature. Indeed, Table 1 shows that the polarity factors of Silochrome S-80 containing a monomolecular layer of cholesteryl pelargonate (0.754 mg m^{-2}) diminish with increasing column temperature.

Table 1. The polarity factors (x, y, z, u, and s) and the conventional chromatographic polarities (P) of sorbents based on silicas and liquid crystals (standard—squalane, t—column temperature).

LC	t, °C	x	y	z	u	s	P
			Silochrome S-80				
—	200*	1.30	7.36	8.05	5.04	9.20	31
—	200	0.40	4.05	5.80	3.15	6.90	8
(III)	100	0.21	5.06	3.43	2.31	2.92	12
(III)	135	0.26	5.16	2.88	2.43	3.80	10
(III)	165	0.30	6.16	2.86	2.23	5.21	6
(II)	63	0.26	4.14	2.93	2.89	—	28
(II)	78	0.17	2.36	2.86	0.84	—	14
(II)	91.5	0.01	1.81	2.10	0.73	—	11
			Chromaton				
(V) **	63	1.55	3.35	2.19	3.78	3.40	28
(V) **	120	1.51	2.96	2.13	3.53	2.67	20
(V) **	150	1.75	2.16	2.21	3.55	2.87	18
(II) ***	63	0.26	4.14	3.03	2.79	—	27
(II) ***	78	0.34	4.70	3.83	3.86	—	29
(II) ***	91.5	0.31	3.40	4.07	3.32	—	15

*A hydroxylated adsorbent carrier was used, while in the remaining cases the carrier was dehydroxylated.

**$a_{LC} = 0.052$ mg m^{-2}.

***$a_{LC} = 0.009$ mg m^{-2}; in the remaining cases $a_{LC} = 0.754$ mg m^{-2}.

The system of Rohrschneider's coefficients constitutes a classification where, apart from the electron donor–electron acceptor activity, account is taken of the proton donor–proton acceptor activity of the phases in relation to the sorbates as well as the orientation interaction between them. Thus the polarity factors of the electron donor and acceptor characterising the retention of benzene (x) and nitromethane (u) diminish sharply on transition of compound (II) from the solid to the liquid crystal state and further to the isotropic liquid. The polarity factors of the proton donor characterising the retention of ethanol (y) change sharply on transition of this liquid crystal from the solid to the mesomorphic state.

The conventional chromatographic polarity of this sorbent (Table 1), which we estimated in relation to a specific pair of compounds (benzene–cyclohexane), also decreases with increase of column temperature. On the same liquid crystal deposited on the inert carrier Chromaton, higher polarity factors are observed at the point corresponding to the transition of the liquid crystal from the solid to the mesomorphic state (78 °C); the retention characteristics, particularly the retention times, then increase by a factor of ~5. At 78 °C the conventional chromatographic polarity is also a maximum.

Comparison of the polarity factors on hydroxylated and particularly on dehydroxylated Silochromes with those for the same Silochromes modified by liquid crystals shows that on the latter the polarity factors decrease markedly, especially the polarity factor z (for ethyl methyl ketone) characterising the orientational interaction. Among the initial Silochromes, a high capacity for orientational interaction has been observed for the hydroxylated Silochrome with an intact coating of hydroxy-groups on its surface, which is classified as a type II adsorbent in Kiselev's classification[92]. While the polarity factors s are exceptionally high, the constant a, characterising the dispersion interaction on the hydroxylated Silochrome, is low. A change in the chemical properties of the surface of hydroxylated Silochrome, namely its dehydroxylation (by heat treatment at 1000 °C) and modification with liquid crystals, leads to a sharp decrease of all the polarity constants.

Together with the Rohrschneider method, whereby one can take into account different intermolecular interactions, Brown's method[87] has been applied. Brown was the first to apply the triangular Gibbs–Roozeboom diagram to gas chromatography for a clear estimate of the properties of the stationary phases. This method provides for the use of a triangular graph along the axis of which one plots the retention fractions representing the ratios of the specific retention volume of one of the reference sorbates to the sum of the volumes of three reference sorbates. The following systems have been used for the latter: n-hexane–ethanol–ethyl methyl ketone or n-hexane–nitromethane–pyridine, i.e. nonpolar compound—electron donor–electron acceptor systems.

When the retention of all the elements is determined from a single chromatogram, the retention fraction can be calculated directly from the corrected retention times (t_r):[93]

$$F = t_r/(t_r' + t_r'' + t_r''') . \qquad (2)$$

For the initial and liquid crystal-modified silicas, the retention fraction of ethyl methyl ketone is greatest; consequently, the donor–acceptor interaction makes the main contribution to the retention. In addition, we demonstrated the possibility of using pyridine, a stronger electron donor, and nitromethane, a stronger electron acceptor, as reference sorbates together with n-hexane. For all the sorbent specimens, the retention fractions of pyridine are highest, which again demonstrates the dominant contribution of sorbate–sorbent donor–acceptor interactions to the retention.

Table 2. The polarity factors of certain stationary phases and sorbents based on Chromaton and SLC (V).

SP, sorbent	t, °C	x	y	z	u	s
OV-17	100	2.08	3.85	2.62	5.33	3.45
Sorbent	63	1.55	3.35	2.19	3.78	3.40
SKTF-100	100	1.57	4.96	2.05	3.13	2.47
Sorbent	120	1.51	2.96	2.13	3.53	2.67
OS-124	100	1.75	2.27	2.34	3.26	2.84
Sorbent	150	1.75	2.16	2.12	3.55	2.87

In order to estimate the possibility of the practical application of the polarity constants found for sorbents based on silicas and liquid crystals, it is necessary to compare the results with the literature data for known stationary phases. Such a comparison makes it possible to discover analogues of stationary phases and to illustrate the possibility of replacing the latter by sorbents based on silicas and liquid crystal systems. For comparision, use was made of data of

Subina[94], who characterises in terms of polarity the stationary phases most frequently used in gas chromatographic practice. As an illustration, Table 2 presents some of these data. It shows that the sorbent based on Chromaton and liquid crystal (IV) in a single chromatographic column at different temperatures and hence in different phase states can replace three sorbents: polyphenyl ester OS-124, SKFT-100, and OV-17.

Thus the use of liquid crystals as stationary phases makes it possible to reduce the number of stationary phases used in gas chromatography without diminishing the range in which selectivity can be regulated. Furthermore, the assessment of silica adsorbents and modified sorbents based on them, carried out on the basis of the retention characteristics of reference compounds, permits a well founded approach to the selection of a modified sorbent for the solution of a specific analytical problem.

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