

# Chromatographic properties of graphitized thermal carbon black modified with a monolayer of liquid crystal

V. I. Nazarova\* and K. D. Shcherbakova

*Laboratory of Adsorption and Chromatography, Chemistry Department, Lomonosov State University, 119899 Moscow (USSR)*

O. A. Shcherbakova

*Institute of Chemistry of Nonaqueous Solutions, Academy of Sciences of the USSR, Ivanovo (USSR)*

---

## ABSTRACT

Data obtained by chromatography, adsorption from solution and theoretical calculations show that a monolayer of liquid crystal adsorbed on the surface of graphitized thermal carbon black (GTCB) has an orientational order that is analogous to the mesomorphic state of the substance. A decrease in the adsorption potential and an increase in the general structural selectivity in the separation of polynuclear aromatic and partially hydrogenated compounds were observed for the modified sorbent. This is due to the influence of the liquid crystal monolayer on the adsorption of the studied substance on the one hand, and to the influence of GTCB on the monolayer on the other. The order of elution of isomeric polynuclear hydrocarbons on the modified and unmodified surfaces is the same, which makes it easier to identify the investigated isomeric mixtures.

---

## INTRODUCTION

One of the most interesting possibilities of chromatography is in elucidating the relationship between retention and the molecular structure of the compounds under investigation. In gas chromatography on the non-specific monoatomic adsorbent graphitized thermal carbon black (GTCB) such a relationship has been demonstrated by many workers [1,2]. This forms the basis of the Kiselev and Poshkus method of studying of molecular structure [3,4].

In gas-liquid chromatography, the relationship between retention characteristics and molecular structure is much more complicated [5–9]. Nevertheless, when a liquid crystal material is used as a stationary liquid phase there is still sufficient sensitivity to the form and geometric size of the adsorbed molecules. The structural selectivity in this instance is due to the ordering of the mesophase. According to Witkiewicz [10], long and plane molecules can easily enter the lattice of the liquid crystal while

non-linear and non-planar molecules cannot penetrate easily between anisotropic molecules of the mesogen and, hence they pass through the column more quickly.

It has been established that the state of a liquid crystal stationary phase is defined by the nature of the support and the character of its surface, the orienting influence of which on the structure of the immobile layer being greater in this instance than with traditional liquid stationary phases [10–12]. With inert supports, and also with active supports, the sensitivity of the layer to the molecular structure of adsorbates depends on the amount of liquid crystal deposited [13–15].

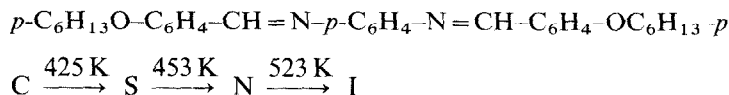
It has been observed [16] that there is a connection between conformational changes and electronic structures of molecules with different types of ordering in the mesophase. Owing to the short-range surface specific and non-specific interactions in the first adsorption layer, liquid crystal molecules applied as a monolayer on an active support of silica (glass, Silochrome) or on to split graphite form

highly oriented layers [17]. By means of scanning tunnelling microscopy, some data on the state of the liquid crystal monolayer on split graphite have been obtained [18]. The position and orientation of molecules in the liquid crystal lattice were determined [18]. The overlapping of terminal groups in the monolayer film is weaker than in the bulk. It was also noted [18] that the structure of the layer is more likely to be molecular than of liquid crystalline type. Hence the use of the mesophase notion is inappropriate and there are no mesomorphic transitions in this instance. High structural selectivity of a monolayer of liquid crystal of cholesteric type on hydroxylated and dehydroxylated Silochrome was found in the gas chromatographic separation of xylene isomers [19].

The aim of this work was to determine the structural selectivity of a monolayer of liquid crystal of nematic type applied to GTCB. The adsorption of molecules on a non-porous homogeneous surface of GTCB depends on their geometry and polarizability. The same tendency was observed in the papers cited for the adsorption of molecules on a liquid crystal film. However, GTCB has a high adsorption potential and requires high working temperatures; GTCB pellets can easily be ruined. In addition, the majority of the liquid crystal exists in the nematic state in a narrow temperature interval. Hence, with the known advantages and disadvantages of GTCB and of liquid crystal stationary phases, it was considered of interest to modify GTCB with a liquid crystalline substance. Studies were made of the influence of non-specific adsorption of the support on the anisotropic properties of the monolayer on the one hand, and the influence of the monolayer on the adsorption properties of GTCB on the other.

#### EXPERIMENTAL

Sterling MT 3100 D4 GTCB (Cabot, Boston, MA, USA) with a specific surface area of 7.6 m<sup>2</sup>/g was used as the adsorbent. For application of a monolayer we chose a high-temperature liquid crystal of the nematic type, bis(hexyloxybenzylidene) phenylendiamine (BHOBPDA), trademark H-75 (USSR):



where C = crystal state, S = smectic state, N = nematic state and I = isotropic liquid. This compound has a low saturated vapour pressure and a wide temperature interval of the mesophase.

The calculation of the amount of liquid crystal which corresponds to a monolayer is based on the Van der Waals size of the molecules and on the following circumstances: (a) liquid crystal molecules have no active terminal groups; (b) the maximum gain in energy is for horizontal packing of the molecules; and (c) there are no pores on the GTCB surface. The area occupied by one liquid crystal molecule on the GTCB surface was found to be 185 Å, and the amount of liquid crystal corresponding to monolayer covering was 0.9 μmol/m<sup>2</sup> according to calculations. This value was proved experimentally by adsorption from solution. The equilibrium concentrations were determined with a Model SF-4A spectrophotometer (USSR).

Gas chromatographic measurements were carried out on a Chrom-5 analytical chromatograph (Czechoslovakia) equipped with a flame ionization detector and modified for physico-chemical investigations [20] and on an LKhM-8 MD chromatograph (USSR).

The following micropacked columns (MPC) were used: (1) GTCB modified with a monolayer of BHOBPDA, 45 cm × 1 mm I.D., pellet fraction 0.16–0.18 mm, mass of GTCB 0.5482 g and of liquid crystal 0.0018 g; (2) modified Chromaton N AW, pellet fraction 0.16–0.18 mm, 5 wt.% of liquid crystal, columns 25 cm × 1 mm I.D. and 90 cm × 0.75 mm I.D., mass of the packing 0.0841 g and 0.2029 g, respectively. The liquid crystal was precipitated on the GTCB and Chromaton N AW from dichloromethane solution under constant vibration followed by conditioning by heating in a flow of nitrogen.

The chromatographic sorption characteristics of the investigated compounds on the modified GTCB were compared with those obtained on unmodified GTCB [21] and in the bulk of the liquid crystal applied to Chromaton N AW.

Isomeric mixtures of partially or fully hydrogenated aromatic compounds were used as ad-

sorbates. The injection of adsorbates into the column was performed with 10% solutions in ethanol or benzene without splitting of the gas flow.

## RESULTS AND DISCUSSION

The obtained adsorption isotherm has a saturation region, which corresponds to a monolayer. The amount of liquid crystal is  $0.9 \mu\text{mol}/\text{m}^2$ . The dependences of the logarithms of the retention volumes of phenanthrene and anthracene on reciprocal of temperature in the bulk phase of the liquid crystal on Chromaton N AW are presented in Fig. 1. The character of these curves is in agreement with the common concept of phase transitions in liquid crystals. The three regions of the different phase states of BHOBPDA can easily be distinguished, namely the crystalline, smectic and nematic states. The transition of the liquid crystal from crystal to smectic is accompanied by a decrease and that to the nematic state by an increase in retention. A further increase in temperature leads to a decrease in retention.

The fact that the temperatures of the phase transitions of the pure liquid crystal and liquid crystal applied to Chromaton coincide proves that at the given degree of impregnation the inert support does not influence the properties of liquid crystal phase. The separation of the sorbates is due to the difference in the enthalpy of dissolution of the sorbates in the liquid crystal bulk. The maximum

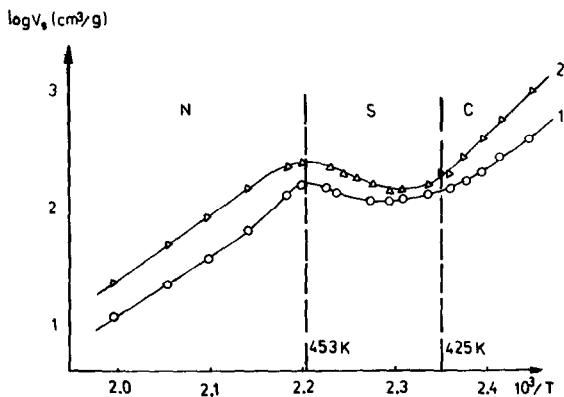


Fig. 1. Temperature dependence of the retention volumes of (1) phenanthrene and (2) anthracene on Chromaton N AW with 5% liquid crystal.

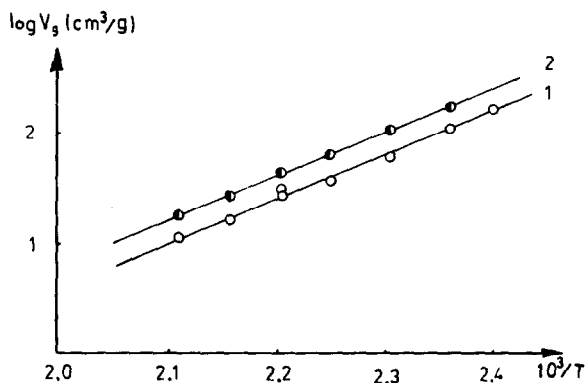


Fig. 2. Temperature dependence of the retention volumes of (1) phenanthrene and (2) anthracene on GTCB modified with a liquid crystal monolayer.

structural selectivity,  $\alpha = V_g(\text{anthracene})/V_g(\text{phenanthrene})$  corresponds to the nematic state.

As can be seen from Fig. 2, there are no bends on the curves of the dependences of the logarithms of the retention volumes of phenanthrene and anthracene on the GTCB surface modified with a monolayer of BHOBPDA. Hence no phase transition of the liquid crystal monolayer on the GTCB surface takes place and its physical characteristics change continuously.

In the investigated temperature range, a high selectivity of separation of these components was observed. In addition to anthracene and phenanthrene, acenaphthene, acenaphthylene, fluorene and pyrene were also studied on modified GTCB. Their retention characteristics are given in Table I for different stationary phases for comparison.

It can be seen from Table I that the retention values on modified GTCB are lower than those obtained for adsorption on unmodified GTCB, and also for dissolution in the liquid crystal. The retention values of aromatic compounds on the unmodified GTCB at 473 K were obtained by extrapolation. The decrease in the adsorption potential on modified GTCB can be related to the increase in the distance between the interacting molecular centres of the adsorbate and the support by the thickness of the layer. The retention values also reflect the contribution of the specific interactions between molecules of the adsorbate and those of the liquid crystal. Here the presence of benzene rings in the

TABLE I

RETENTION VOLUMES,  $V_g^{473}$  (473 K), INTERNAL ENERGY,  $-\Delta U$ , AND SELECTIVITY COEFFICIENT,  $\alpha$ , MEASURED ON DIFFERENT STATIONARY PHASES

$$\alpha = V_g(\text{anthracene})/V_g(\text{phenanthrene}).$$

Substance	Liquid crystal		GTCB		GTCB + liquid crystal	
	$V_g^{473}$ ( $\text{cm}^3/\text{g}$ )	$-\Delta U$ (kJ/mol)	$V_g^{473}$ ( $\text{cm}^3/\text{g}$ )	$-\Delta U$ (kJ/mol)	$V_g^{473}$ ( $\text{cm}^3/\text{g}$ )	$-\Delta U$ (kJ/mol)
Acenaphthene	822	55	1751	91	16.7	76
Acenaphthylene	836	51	1975	93	6.7	64
Fluorene	384	38	8334	79	15.5	79
Pyrene	5380	43	—	—	83.3	64
Phenanthrene	1194	45	53662	97	19.5	77
Anthracene	820	42	44017	97	11.8	76
$\alpha$	1.45		1.22		1.65	

liquid crystal was responsible for the high affinity to aromatic molecules of the sorbates.

The increase in selectivity obtained in the separation of phenanthrene and anthracene on modified

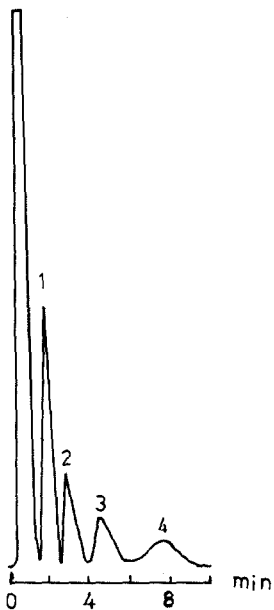


Fig. 3. Chromatogram of a mixture of tetracyclic aromatic hydrocarbons in a micropacked column with 5% liquid crystal on Chromaton N AW, pellet fraction 0.16–1.18 mm, column 25 cm  $\times$  1 mm I.D., temperature 443 K, mass of adsorbent 0.841 g, inlet pressure  $1.92 \cdot 10^5$  Pa (1.9 atm), carrier gas nitrogen, flow-rate 10 ml/min. Peaks: 1 = benzenanthracene; 2 = triphenylene; 3 = pyrene; 4 = chrysene.

GTCB reflects the effect of the action of the adsorption field of GTCB and of the monolayer of BHOBPDA, which is in a structured state similar to the mesomorphic state of a bulk phase. It should be noted that the order of elution on the unmodified GTCB and in the bulk phase of the liquid crystal on Chromaton coincides for nearly all the compounds. The selectivity of the mesomorphic phase to aromatic compounds is high, as can be seen, for example, in the separation of a mixture of tetracyclic aromatic hydrocarbons in the short micropacked column (Fig. 3).

The structural selectivity of the liquid crystal bulk phase to the isomers of perhydro compounds in the absence of specific interactions is not so high. In this instance the separation of the isomers is due only to the difference in their molecular structures. On the 90-cm column with liquid crystal stationary phase applied to Chromaton N AW the mixture of isomers of perhydroanthracene was not separated completely (Fig. 4a), whereas on the unmodified GTCB such a separation is possible (Fig. 4b). The identification of peaks was based on mass composition in the case of their separation on 5 wt. % liquid crystal (Fig. 4a). The separation of the same mixture on modified GTCB in the 45-cm column with temperature programming is shown in Fig. 4c. The order of elution for all the above columns coincides. For the separation of perhydroanthracene isomers on modified GTCB in comparison with unmodified GTCB, the selectivity estimated with only the first two peaks

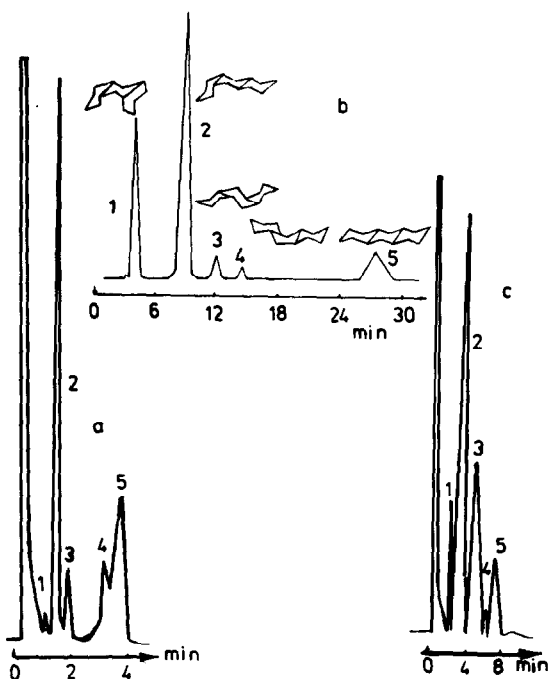


Fig. 4. (a) Chromatogram of the mixture of perhydroanthracene isomers in a micropacked column with 5% liquid crystal on Chromaton NAW; column 90 cm  $\times$  1 mm I.D., temperature 458 K, mass of adsorbent 0.2029 g, inlet pressure  $1.92 \cdot 10^5$  Pa (1.9 atm), carrier gas nitrogen, flow-rate 3 ml/min. (b) Separation of perhydroanthracene isomers in a micropacked column with unmodified GTCB [21]; column 1.2 m  $\times$  1 mm I.D., carrier gas hydrogen, flow-rate 10 ml/min, flame ionization detection, mass of GTCB 0.788 g, inlet pressure  $2.12 \cdot 10^5$  Pa (2.1 atm). (c) Separation of perhydroanthracene isomers in a micropacked column with GTCB modified with liquid crystal; column 45 cm  $\times$  1 mm I.D., temperature programmed from 433 to 443 K starting at the 4th minute, carrier gas nitrogen, flow-rate 10 ml/min, mass of adsorbent 0.55 g, inlet pressure  $1.92 \cdot 10^5$  Pa (1.9 atm), GTCB fraction (as in b) 0.16–0.18 mm. Peaks: 1 = *cis-syn-cis*; 2 = *cis-syn-trans*; 3 = *cis-anti-cis*; 4 = *trans-anti-trans*; 5 = *trans-syn-trans*.

being taken into account is slightly lower and the working temperature necessary for the separation decreases (by 70–80 K).

The use of GTCB modified with a liquid crystal monolayer can be successful for the separation of technological mixtures obtained by hydrogenation of high-boiling polyaromatic compounds, the result of which is the formation of isomeric compounds with different degrees of hydrogenation. We obtained a complete separation of a mixture of deca-

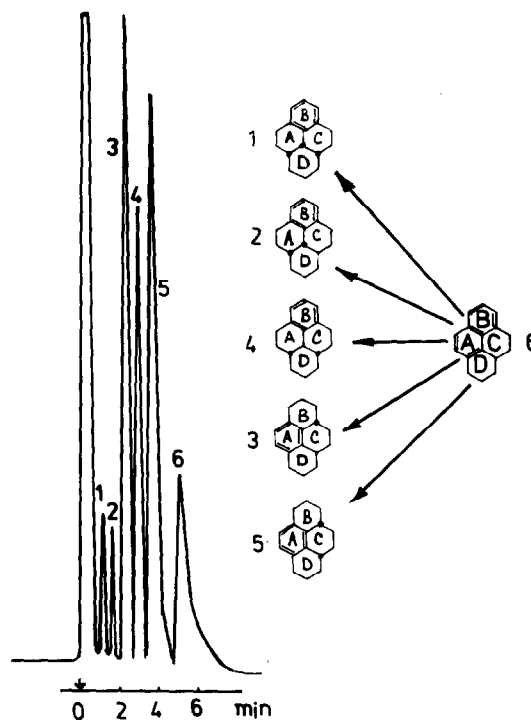


Fig. 5. Separation of a mixture of perhydropyrene isomers in a micropacked column with GTCB modified with a liquid crystal monolayer. Temperature 453 K, other conditions as in Fig. 4c.

hydropyrenes (obtained by hydrogenation of hexahydropyrene at low temperatures), as shown in Fig. 5. In this instance theory predicts the existence of five possible isomers. The identification of the peaks of this mixture was performed as described previously [20] according to the model concepts of their molecular structures and using the sum of the distances of their atoms from the plane surface of the adsorbent ( $\sum \tau_i$ ). According to the decreasing order of this value, the first to elute from the column with GTCB modified with BHOBPDA should be the isomer with the molecule containing an incompletely hydrogenated B-ring and the rings in the row A–D–C have *cis* linkages, *i.e.*, hydrogen atoms at carbon atoms 8, 12 and 16 are situated at one side of the system of rings. This isomer, ADC-*cis*-decahydro-B-pyrene, has the most bent form of the molecule and the maximum sum of distances from the adsorption field plane,  $\sum \tau_i$ . The other isomers are eluted according to the decrease of this sum. The isomer ADC-*cis*, *trans*-decahydro-B-pyrene is the

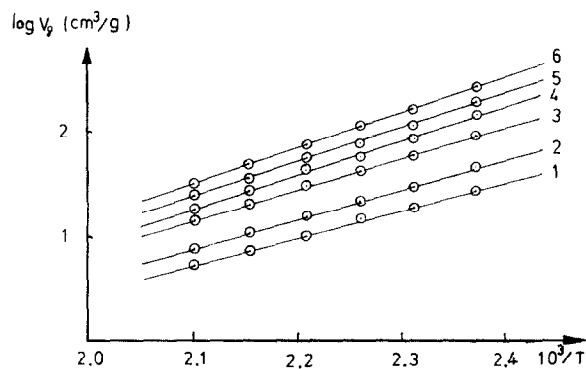


Fig. 6. Temperature dependence of the retention volumes of perhydropyrene isomers in a 45-cm micropacked column with GTCB modified with a liquid crystal monolayer. The curve numbers correspond to the peak numbers in Fig. 5.

second to elute. In its molecule the B-ring is incompletely hydrogenated and the A-D-C rings have *cis* and *trans* linkages. The third peak on the chromatogram belongs to the isomer in which the A-ring is incompletely hydrogenated and the B-C-D rings have *trans*, *cis* linkages, i.e., to BCD-*trans*,*cis*-decahydro-A-pyrene. The fourth peak corresponds to ADC-*trans*,*trans*-decahydro-B-pyrene and the fifth to the isomer with an incompletely hydrogenated A-ring and *cis* linkages of the B-C-D rings. The sixth peak belongs to the initial compound hexahydropyrene, the molecule of which has the most planar structure.

The separation of isomers of this mixture on OV-1 liquid stationary phase has been published [22]. The temperature necessary for the elution of isomers of this mixture on carbon black modified with liquid crystal is lower than that for their elution on unmodified carbon black by 150–180 K. The chromatogram in Fig. 5 was obtained with a 45-cm micropacked column of GTCB modified with BHOBPDA. The high selectivity of the separation on this sorbent can be explained by the overall contribution of non-specific dispersion and specific interactions caused by the presence of the aromatic ring in an A or B position in molecules of decahydropyrenes. The selectivity of separation of this mixture on modified GTCB is higher than that on the liquid crystal phase.

The curves of the dependence of  $\log V_g$  on the reciprocal of temperature are presented in Fig. 6. As it can be seen, a high selectivity is observed over the

whole interval of temperatures studied. This confirms the assumption about high orientational ordering and stability of the liquid crystal monolayer applied to a homogeneous graphite surface. The column with GTCB modified with BHOBPDA has been used for 1 year without changes in its properties.

## CONCLUSIONS

Adsorption from solution and theoretical calculations have shown that the amount of liquid crystal adsorbed on a GTCB surface corresponds to a monolayer. The molecular orientational ordering of a two-dimensional BHOBPDA film is similar to the mesomorphic state of a bulk phase. There are no phase transitions in the adsorbed liquid crystal monolayer and the working temperature range is widened. Comparison of the retention characteristics obtained for polynuclear hydrocarbons in chromatographic columns containing unmodified GTCB, bulk phase of BHOBPDA and GTCB modified with a BHOBPDA monolayer shows that the decrease in adsorption potential and working temperature is due to the action of the liquid crystal monolayer. The structural selectivity of GTCB modified with liquid crystal for the separation of aromatic and partially hydrogenated isomeric polynuclear compounds is higher than that with unmodified GTCB or with the liquid crystalline bulk phase.

GTCB modified with a monolayer of BHOBPDA or other liquid crystals with the use of more effective capillary columns appears promising for the separation of complex isomeric mixtures of high-boiling compounds. It has been established that for GTCB modified with a liquid crystal monolayer the relationship between the retention values of hydrocarbons and their molecular structures is of the same character for unmodified GTCB.

## REFERENCES

- 1 A. V. Kiselev and Ya. I. Yashin, *Adsorbtsionnaya Gazovaya i Zhidkostnaya Khromatografiya (Adsorption Gas and Liquid Chromatography)*, Khimiya, Moscow, 1979.
- 2 A. V. Kiselev, *Molekulyarnye Vzaimodeistviya v Adsorbtsii i Khromatografii (Molecular Interactions in Adsorption and Chromatography)*, Vysshaya Shkola, Moscow, 1986.
- 3 A. V. Kiselev and D. P. Poshkus, *Faraday Discuss. Chem. Soc.*, 15 (1980) 13.

- 4 A. V. Kiselev, in Ya. M. Kolotyркиn (Editor), *Sovremenniyе Problemy Fisicheskoi Khimii (Modern Problems of Physical Chemistry)*, Khimiya, Moscow, 1982, p. 180.
- 5 A. V. Ladon, *Chromatographia*, 4 (1971) 171.
- 6 R. V. Golovnya and D. N. Grigoryeva, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 3 (1987) 596.
- 7 W. Engewald and L. Wennrich, *Chromatographia*, 9 (1976) 540.
- 8 V. M. Nabivach and W. E. Vasiliev, *Zh. Fiz. Khim.*, 62 (1988) 1873.
- 9 A. Voelkel, *J. Chromatogr.*, 464 (1989) 251.
- 10 Z. Witkiewicz, *J. Chromatogr.*, 251 (1982) 311.
- 11 Oweimreen Ghassan Andrawes, *Mol. Cryst. Liq. Cryst.*, 68 (1981) 257.
- 12 K. Shoji, T. Ishiji and M. Takeda, *J. Chem. Soc. Jpn.*, 4 (1980) 557.
- 13 J. Rayss and F. Waksmundzki, *J. Chromatogr.*, 292 (1984) 207.
- 14 W. Marciniak and Z. Witkiewicz, *J. Chromatogr.*, 207 (1981) 333.
- 15 W. Marciniak and Z. Witkiewicz, *J. Chromatogr.*, 324 (1985) 299.
- 16 A. C. Sarkisyan and S. M. Yayloyan, *Zh. Strukt. Khim.*, 30 (1989) 173.
- 17 C. S. Mullin, P. Guyot-Sionnest and R. Shen, *Phys. Rev. A*, 39 (1989) 3745.
- 18 D. P. E. Smith, H. Horber, Ch. Gerber and G. Binnig, *Science*, 245 (1989) 43.
- 19 S. P. Vetrova, N. P. Karabanov and Ya. I. Yashin, *Dokl. Akad. Nauk SSSR*, 250 (1980) 1165.
- 20 A. V. Kiselev, V. I. Nazarova and K. D. Shcherbakova, *Chromatographia*, 14 (1981) 148.
- 21 A. V. Kiselev, V. I. Nazarova and K. D. Shcherbakova, *Chromatographia*, 18 (1984) 183.
- 22 G. Mann, A. Sicker, R. Herzschuh, W. Engewald and K. Praefcke, *J. Prakt. Chem.*, 331 (1989) 267.