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COMPARISON OF THE PROPERTIES OF LIQUID CRYSTAL FILMS ON SILICA GEL AND ON A GRAPHITE SURFACE

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SUMMARY

The effect of the solid surface on the properties of liquid crystal films was studied. The results show that the structure of such films depends strongly on the kind of solid support. An additional phase transition, other than solid-nematic and nematic-isotropic liquid, has been found in films of liquid crystals on a graphite surface. At temperatures higher than the nematic-isotropic liquid transition, the surface film on silica gel is probably the monolayer composed of horizontal molecules. The structure of the surface film on graphite is more complicated.

INTRODUCTION

Since the early 1960s a great increase has been observed in the application of liquid crystals as stationary phases in gas chromatography. This type of stationary phase is very useful for many difficult analyses, especially for the separation of isomers. The main factor affecting successful separations is the compatibility of the dimensions of the sample molecules and the structure of the liquid crystal mesophase. As more than 200 liquid crystals characterized by different structures of the mesophase have been used in chromatography, it is possible to find a suitable compound for almost every analysis¹.

Nematic liquid crystals have the largest temperature range of mesophase existence. This range, and the degree of molecular ordering, may be strongly affected by the surface of the solid support. There are many papers describing these effects due to the presence of a solid surface beneath the liquid crystal film¹⁻⁷. Generally, one can state that "active" supports, *e.g.*, silica gel or Chromosorb P NAW, increase the temperature range of mesophase existence, whereas the problem of establishing the structure of the liquid crystal film on a solid support remains unsolved.

In previous work⁷ we found that the effect of the adsorption forces of Chromosorb P NAW on the liquid crystal film had a range of about 2 nm and depended on temperature. It was also shown that the chromatographic properties of the film influenced by the support surface were different than those of bulk liquid crystal. In this paper we report the results of some investigations on the structure and properties of liquid crystal films deposited on very different surfaces, *viz.*, silica gel and graphite.

EXPERIMENTAL

The liquid crystal used as the stationary phase was *p*-butyl-*p*'-hexanoylazo-benzene, $p\text{-C}_4\text{C}_9\text{-C}_6\text{H}_4\text{-N}=\text{N-C}_6\text{H}_4\text{-[CO(CH}_2)_4\text{CH}_3\text{]-}p'$ (PHPB). The solid-nematic phase transition in this compound takes place at 58.5°C and the second transition, nematic phase to isotropic liquid, occurs at 65°C .

The solid supports of PBHB were silica gel and graphite with specific surface areas of 16.1 and $3.02\text{ m}^2/\text{g}$, respectively. The amount of ash in graphite was determined to be below $3 \cdot 10^{-3}\%$. Fractions of 60–80 mesh of both adsorbents were used to prepare column packings with PBHB. Glass columns were 1 m long and 4 mm I.D. The measurements of the retention volume (V_s)⁷ were performed on a Chrom 4 gas chromatograph (Laboratorni Přístroje, Prague, Czechoslovakia).

The test substances used in chromatographic measurements were analytical-reagent grade *n*-octane and toluene (Reakhim, U.S.S.R.).

RESULTS AND DISCUSSION

PBHB films on a silica gel surface

The results obtained by the "inverse" gas chromatographic method are usually

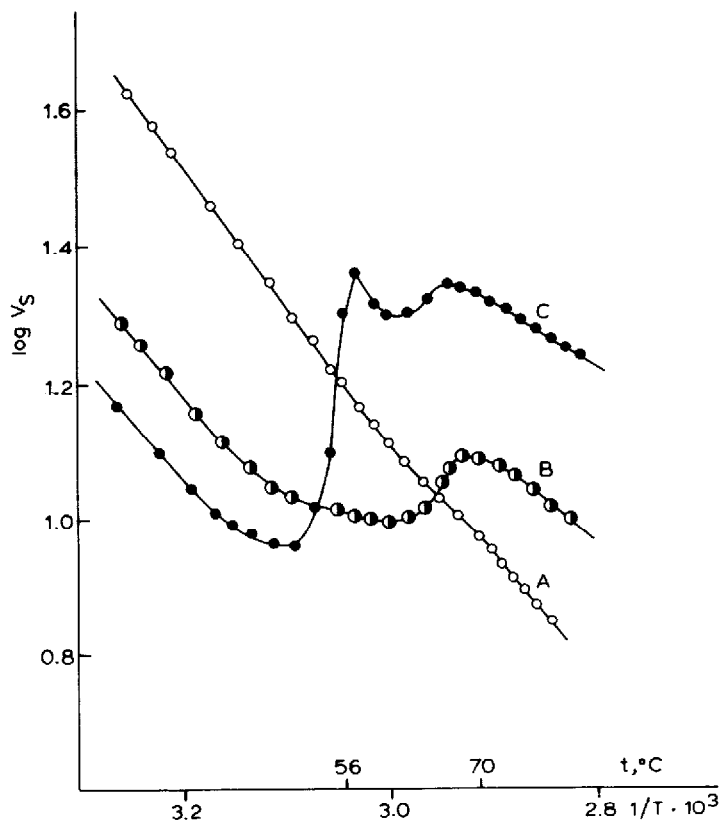


Fig. 1. $\log V_s$ vs. $1/T$ plots for *n*-octane. The column packings were composed of silica gel covered with (A) 1.3%, (B) 5% and (C) 12.1% of PBHB.

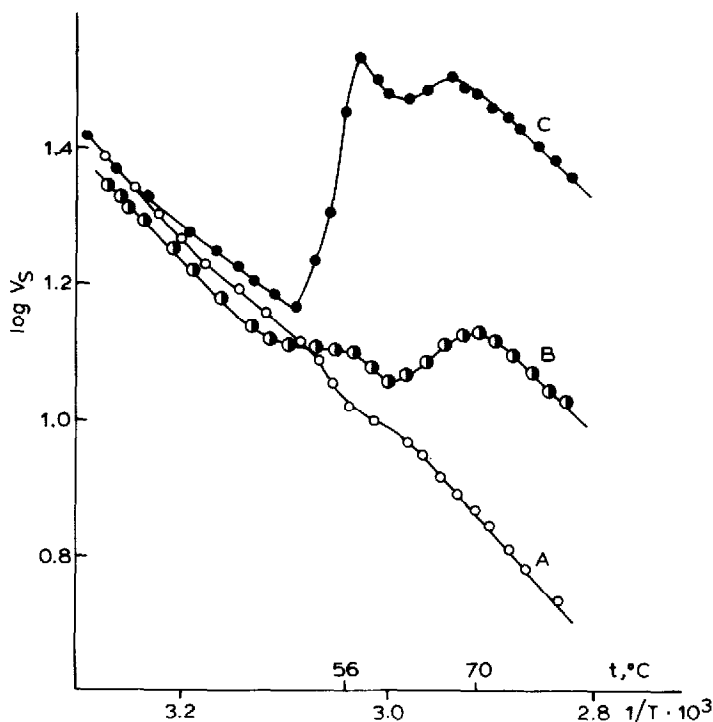


Fig. 2. Log V_S vs. $1/T$ plots for toluene. Column packings as in Fig. 1.

presented as plots of the retention volume, V_S , versus $1/T$. Such diagrams, for *n*-octane and toluene, are presented in Figs. 1 and 2. The column packings were composed of silica gel and different amounts of PBHB. The steps in the curves presented are connected to the solid-nematic and nematic-isotropic liquid phase transitions taking place in the film of liquid crystal on the silica gel surface. The temperatures of the maxima of these steps, measured on the $\log V_S = f(1/T)$ diagram obtained for Gas-Chrom RZ (DMCS treated) and 5% (w/w) of PBHB, are 58.4 and 66°C, *i.e.*, very close to the temperatures of the phase transitions in PBHB determined by the thermo-optical method. This means, according to the data published by Chow and Martire⁴, that the silanized surface of a solid support does not influence the structure and properties of a liquid crystal film.

When silica gel is used as the liquid crystal support, the influence of its surface on the PBHB film is very clear and appears as the broadening of the temperature range of mesophase existence, Δt_m . The thinner the layer of PBHB on the silica gel surface, the greater is the broadening of Δt_m (Table I). The limits of Δt_m are determined by the maxima on curves B and C in Figs. 1 and 2. These temperatures and the Δt_m values corresponding to them are given in Table I. It is worth noting that the clear nematic-isotropic liquid phase transition occurs at $\tau = 3\%$, whereas the solid-nematic transition is detected with injected substances with twice the amount of PBHB on the silica gel surface (τ is the ratio of the mass of PBHB to that of the solid support). Small steps may be observed on curves A in Figs. 1 and 2, but they are too small to provide a basis for the determination of the phase transition

TABLE I

TEMPERATURES (°C) OF PHASE TRANSITIONS IN PBHB FILMS DEPOSITED ON A SILICA GEL SURFACE AS A FUNCTION OF THE AMOUNT OF PBHB, τ

Test substance		τ (%)					
		1.3	3.0	5.0	7.68	12.08	16.04
n-Octane	In solid	—	—	—	—	—	—
	Solid-nematic	—	—	—	55.8	57.3	57.9
	Nematic-isotropic liquid	—	69.9	70.6	70.3	66.9	66.2
	Δt_m	—	—	—	14.5	9.6	8.3
Toluene	In solid	—	—	—	—	—	—
	Solid-nematic	—	—	55.4	55.7	57.2	57.9
	Nematic-isotropic liquid	—	71.5	70.4	69.6	67.3	66.2
	Δt_m	—	—	15.0	13.9	10.1	8.3

temperature. It is interesting that the increase in the range of the nematic phase existence is caused by the decrease in the temperature of the solid-nematic phase transition and by the increase in the melting temperature of PBHB. Both effects are the greater the thinner the PBHB layer is on the silica gel surface (Table I). Kubelka⁸, Berezin *et al.*⁹ and Brun *et al.*¹⁰ have stated that the melting point of thin films of liquids (or liquid in the pores of a solid) may be significantly lower than that of a liquid in the bulk state. Perhaps the same phenomenon is responsible for the decrease in the temperature of the solid-nematic phase transition. On the other hand, the increase in the temperature of the nematic-isotropic liquid transition is probably caused by the stabilizing influence of the solid surface on the nematic phase structure^{2,3}.

The facts mentioned above allow one to conclude that the structure of the liquid crystal film on the silica gel surface at $\tau \leq 5\%$ is different than that of the layer of this compound situated further from such a surface. In other words, the influence of the silica gel surface on the liquid crystal layer directly adjacent to this surface is so strong that the occurrence of a solid-nematic phase transition become impossible. The same conclusion may be drawn from the plots of V_S against the amount of PBHB in the column packing (Fig. 3). These diagrams were constructed for three temperatures corresponding to the solid (A), nematic (B) and isotropic liquid (C) states of PBHB. The shape of curves A and B indicates that the retention mechanism of *n*-octane changes with an increase in the amount of PBHB in the column packing. The decrease in V_S values at 39.5°C in the region of coverage 0–6% of PBHB may be explained by progressive deactivation of the silica gel surface and the formation of an ordered layer of liquid crystal. Thus, the retention volumes in this range of τ are defined by the interaction of *n*-octane molecules and the surface of bare silica gel. After the ordered layer of PBHB is formed, the factor deciding the

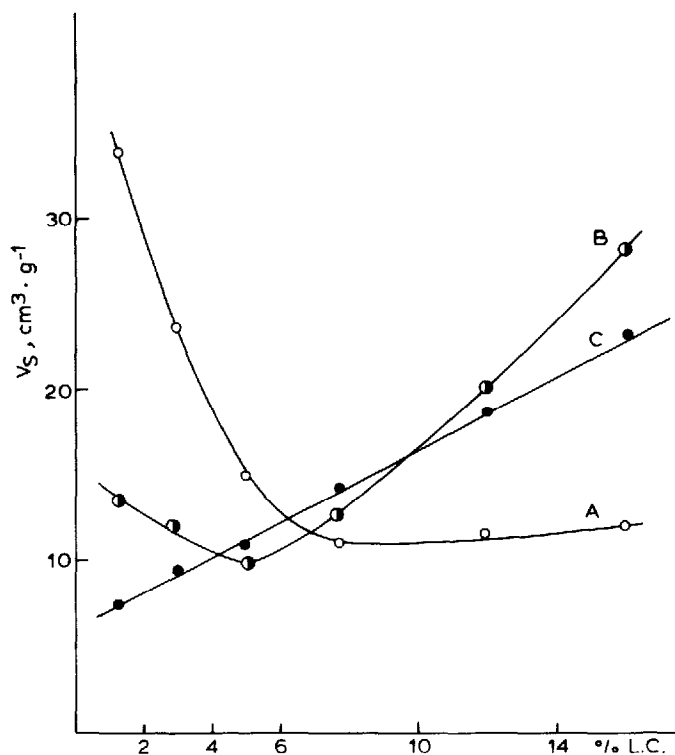


Fig. 3. Plots of V_S vs. the coverage of silica gel. The test substance was *n*-octane. Curve A was determined at 39.5°C, B at 60.1°C and C at 77.7°C. L.C. = liquid crystal.

V_S value is adsorption on PBHB crystals. For this reason, for 6% of PBHB the values of V_S become constant.

The decrease in V_S in the coverage range $0 < \tau < 5\%$ at 60.1°C (curve B) is much smaller than at 39.5°C, but the retention mechanism is probably the same as described above. The subsequent increase in V_S may be explained by the dissolution of *n*-octane in the nematic phase of PBHB. Therefore, at 60.1°C, an ordered surface film is also formed.

The plot of V_S versus τ at 77.7°C is a straight line over the whole range of τ . This means that the retention mechanism does not change; therefore, the whole amount of BBHB is characterized by the same properties. It may be assumed that at this temperature no surface film exists, or, if it is formed under the liquid PBHB, there are very few molecules present in it.

PBHB films on graphite

Figs. 4 and 5 show the plots of $\log V_S = f(1/T)$ for *n*-octane and toluene obtained for column packings composed of graphite and PBHB. The fundamental difference between these plots and those obtained for silica gel covered with PBHB is an additional step at 50–55°C (the temperature at which this step occurs also depends on τ ; cf., Table II). This means that in the PBHB layer on the graphite surface, apart from the solid–nematic and nematic–isotropic liquid transitions, an additional

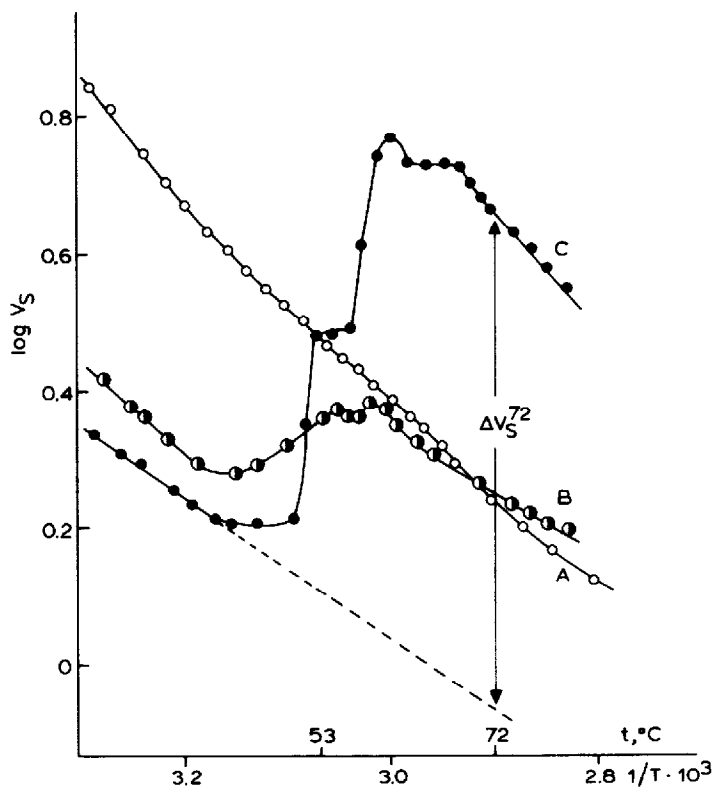


Fig. 4. $\log V_s$ vs. $1/T$ plots for *n*-octane. The column packings were composed of graphite covered with (A) 0.5%, (B) 1.3% and (C) 3% of PBHB.

transition takes place. A similar phenomenon was found by Marciniak and Witkiewicz⁶ for some liquid crystals deposited on silanized supports. Calorimetric investigations proved that in solid PBHB in the bulk state no phase transition takes place at temperatures below 58°C, and therefore the effect observed may be only the result of the influence of the graphite surface on the PBHB film. The data in ref. 6 and those reported here do not enable us to explain fully the reason for the change in the structure of the PBHB film. Perhaps, in the case of graphite, some role is played by the geometrical consistency of the adsorption centres on its surface and the dimensions of the PBHB molecules. Then, just at the solid surface, a film of PBHB molecules may be formed oriented differently than in the layer more distant from this surface. Such a phenomenon was described by Findenegg and co-workers¹¹⁻¹³ in layers of long-chain alcohols and hydrocarbons adsorbed on graphite.

Comparing the shapes of the $\log V_s$ versus $1/T$ plots for *n*-octane and toluene (Figs. 4 and 5) and the data from Tables I and II, the following conclusions may be drawn:

- (1) the nematic-isotropic liquid phase transition in the PBHB film on the graphite surface is detected only for the highest coverages and only with *n*-octane;
- (2) toluene is a "better detector" of the solid-nematic transition but, because

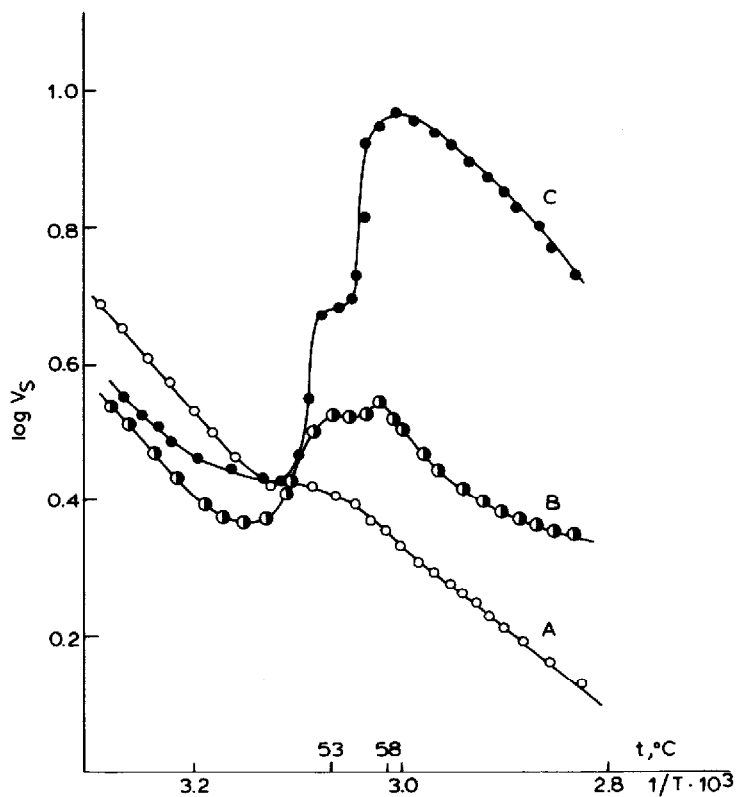

 Fig. 5. $\log V_s$ vs. $1/T$ plots for toluene. Column packings as in Fig. 4.

TABLE II

 TEMPERATURES ($^{\circ}\text{C}$) OF PHASE TRANSITIONS IN PBHB FILMS DEPOSITED ON A GRAPHITE SURFACE AS A FUNCTION OF THE AMOUNT OF PBHB, τ

Test substance		τ (%)					
		0.5	0.9	1.29	2.04	3.01	4.11
n-Octane	In solid	—	55.4	54.7	51.2	52.5	50.1
	Solid-nematic	—	—	58.7	59.6	59.5	59.1
	Nematic-isotropic liquid	—	—	—	—	68.0	67.8
	Δt_m	—	—	—	—	8.5	8.7
Toluene	In solid	—	—	53.6	50.1	52.5	50.2
	Solid-nematic	—	57.2	57.9	58.7	59.0	59.1
	Nematic-isotropic liquid	—	—	—	—	—	—
	Δt_m	—	—	—	—	—	—

TABLE III

VALUES OF τ_f OF PBHB ON SILICA GEL AND GRAPHITE SURFACES, DETERMINED FROM $\log V_S = f(1/T)$ RELATIONSHIPS FOR *n*-OCTANE

Support	τ (% w/w)	τ (g/m ²)	ΔV_S^{72} (cm ³ /g)	τ_f (g/m ²)
Silica gel	12.08	$7.46 \cdot 10^{-3}$	18.97	$4.53 \cdot 10^{-4}$
	7.68	$4.74 \cdot 10^{-3}$	12.99	$3.23 \cdot 10^{-4}$
	5.0	$3.09 \cdot 10^{-3}$	7.57	$3.06 \cdot 10^{-4}$
	3.0	$1.86 \cdot 10^{-3}$	4.13	$3.39 \cdot 10^{-4}$
Graphite	4.11	$13.61 \cdot 10^{-3}$	5.69	$2.42 \cdot 10^{-3}$
	3.01	$9.97 \cdot 10^{-3}$	3.77	$2.48 \cdot 10^{-3}$
	2.04	$6.75 \cdot 10^{-3}$	1.71	$2.70 \cdot 10^{-3}$
	1.29	$4.29 \cdot 10^{-3}$	0.99	$2.46 \cdot 10^{-3}$

this compound does not detect the point of nematic-isotropic liquid transition, it is impossible to determine the Δt_m value;

(3) Δt_m , the temperature range of mesophase existence determined with *n*-octane, is practically the same in the PBHB layers as in bulk liquid crystal (Table-III).

Properties of PBHB layers directly adjacent to the surfaces of silica gel and graphite

Fig. 6 shows $V_S = f(\tau)$ plots for the system *n*-octane-PBHB on graphite. In contrast to the use of silica gel as the liquid crystal support (Fig. 3), even at 77.7°C the film of PBHB on the surface of graphite is preserved. This film is characterized by properties other than those of an isotropic liquid. In a previous paper⁷, taking into account the $V_S/\tau = f(1/\tau)$ plots and the dimensions of a PBHB molecule, it was calculated that the amount of PBHB "imprisoned" in the surface film was from $13 \cdot 10^{-4}$ to $6.4 \cdot 10^{-4}$ g/m², depending on the temperature.

The $\log V_S = f(1/T)$ dependences also permit the calculation of how much PBHB forms an ordered film on the adsorbent surface. From the definition of V_S , the increase in V_S at a given temperature, ΔV_S^t , divided by the specific retention volume at this temperature, V_g^t , gives τ_B , the amount of the stationary phase generating this increase in retention¹⁴. Because the total amount of the stationary phase on the surface of 1 g of the solid support, τ , is known *a priori*, then

$$\tau - \frac{\Delta V_S^t}{V_g^t} = \tau_f,$$

where τ_f is the amount of the liquid stationary phase bonded in the surface film. The value of V_g for *n*-octane at 72°C, determined separately on a column packing composed of Gas-Chrom RZ and 5% (w/w) PBHB, was 167.2 cm³/g. Fig. 4 shows the manner of determination of ΔV_g^t .

Table II gives the values of ΔV_S^{72} and τ_f . The temperature of 72°C is higher than that of any of the phase transitions taking place in PBHB. It appears that the values of τ_f are constant and independent of τ , but depend strongly, on the type of adsorbent surface: in the surface film of PBHB on graphite, about ten times more PBHB molecules are present than on silica gel. This fact shows clearly that the graphite surface has a stronger influence than silica gel on the structure and durability of the PBHB film.

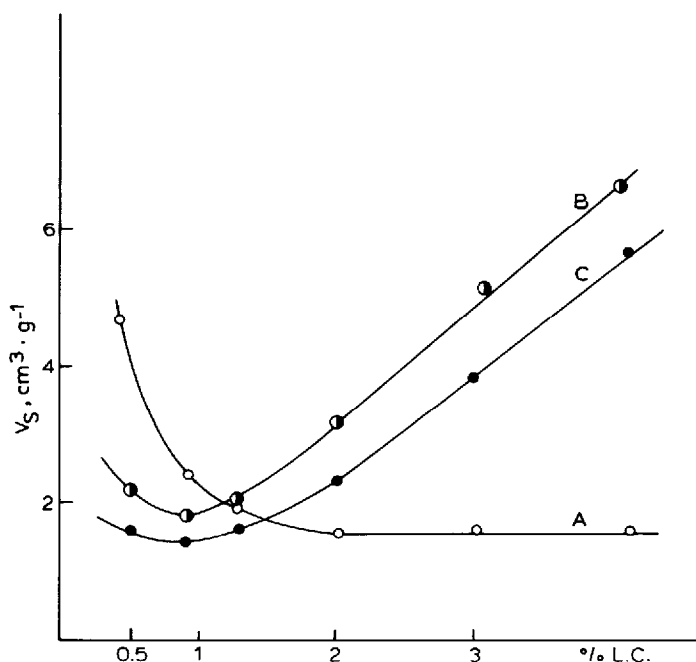


Fig. 6. Plots of V_S vs. coverage of graphite for *n*-octane. Curve A was determined at 39.5°C, B at 63.9°C and C at 77.7°C. L.C. = liquid crystal.

The values of τ_f allow us to calculate the surface area occupied by a single molecule of PBHB in the film directly adjacent to the support surface. This is equal to 0.23 nm² for the film on graphite and 1.93 nm² on the silica gel surface. The cross-sectional area of the PBHB molecule (along its longer axis), according to McClellan and Harnsberger¹⁵, is calculated to be 1.7–2.0 nm². Thus, it is possible that the surface film of PBHB, being in the range of adsorption forces due to the silica gel surface, is a monolayer composed of horizontal molecules, whereas on graphite a polymolecular film is usually formed. The value of 0.23 m² is too small to be the area of the cross-section of the vertically oriented PBHB molecules in relation to the solid surface.

REFERENCES

- 1 Z. Witkiewicz, *J. Chromatogr.*, 251 (1982) 311.
- 2 Z. P. Vetrova, O. A. Vyakhirev, N. T. Karabanov, G. G. Maidatschenko and Ya. I. Yashin, *Chromatographia*, 8 (1975) 643.
- 3 Z. P. Vetrova, N. T. Karabanov and Ya. I. Yashin, *Chromatographia*, 10 (1977) 341.
- 4 L. C. Chow and D. E. Martire, *J. Phys. Chem.*, 73 (1969) 1127.
- 5 J. M. Schnur and D. E. Martire, *Anal. Chem.*, 43 (1971) 1201.
- 6 W. Marciniak and Z. Witkiewicz, *J. Chromatogr.*, 207 (1981) 333.
- 7 J. Rayss, Z. Witkiewicz, A. Waksmundzki and R. Dabrowski, *J. Chromatogr.*, 188 (1980) 107.
- 8 P. Kubelka, *Z. Elektrochem.*, 38 (1932) 611.
- 9 G. I. Berezin, A. A. Kozlov and L. V. Kuznetsova, in B. V. Deryagin (Editor), *Research in Surface Forces*, Vol. 4, Consultants Bureau, New York, 1975, p. 219.

- 10 M. M. Brun, A. Lallemand, J. F. Quinson, B. Martinie, J. Rossignol, B. Rasneur and C. Eyraud, *J. Chim. Phys.*, 70 (1973) 990.
- 11 G. H. Findenegg, *J. Chem. Soc., Faraday Trans. I*, 68 (1972) 1799.
- 12 G. H. Findenegg, *J. Chem. Soc., Faraday Trans. I*, 69 (1973) 1069.
- 13 M. Liphard, P. Glanz, G. Pilarski and G. H. Findenegg, *Prog. Colloid Polym. Sci.*, 67 (1980) 131.
- 14 J. Serpinet, *J. Chromatogr.*, 119 (1976) 483.
- 15 A. L. McClellan, H. F. Harnsberger, *J. Colloid Interface Sci.*, 23 (1967) 577.