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DISTRIBUTION OF THE LIQUID CRYSTAL STATIONARY PHASE ON THE SURFACE OF DIATOMITE SUPPORTS

W. MARCINIAK and Z. WITKIEWICZ*
Institute of Chemistry, Military Technical Academy, 01-489 Warsaw 49 (Poland)
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SUMMARY

The behaviour of a liquid crystal deposited over a wide concentration range on silanized and non-silanized supports was tested. Particular attention was paid to the interaction of the liquid crystal with the surfaces of silanized Chromosorb P, W and G. The dependence of the retention volume of *o*-xylene on the quantity of the phase on the support, as well as the results of investigations of the support porosity, are analysed and the possible distribution of the liquid crystal stationary phase on the supports is given.

INTRODUCTION

The properties of liquid crystal stationary phases depend largely on the kind of support used and on the quantity of the phase deposited[1–4]. We have previously observed a distinct difference in the interaction of the liquid crystal stationary phase with silanized and non-silanized supports[5]. In the case of columns packed with silanized support, we found an additional phase transition of the liquid crystal, not previously described, at a temperature 7°K lower than the melting point determined in the absence of the support. Our observations chiefly concerned packings comprising Chromosorb P, with 0.2–10% (w/w) of the stationary phase.

We have now extended that work to include other silanized supports (Chromosorbs W and G) and a wider range of support coverage (from 0.05%). In this way it was hoped to obtain information that would allow us to elucidate further the distribution of the liquid crystal phase on the support which depends on the nature of the latter and the physico-chemical condition of its surface.

EXPERIMENTAL

The stationary phase used was liquid crystalline 4-cyano-4'-*n*-heptyloxyformyloxyazobenzene:

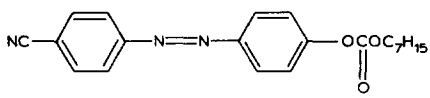

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TABLE I

CHARACTERISTICS OF COLUMNS USED

Column No.	*Chromosorb*	*Weight of packing (g)*	*Amount of stationary phase on support (%)*
1	P AW	11.67	0.05
2	P AW	12.11	0.10
3	P AW	11.77	0.21
4	P AW	12.27	0.41
5	P AW	12.06	0.59
6	P AW	12.07	1.06
7	P AW	12.98	2.09
8	P AW	12.40	4.97
9	P AW	13.39	9.43
10	P AW DMCS	11.04	0.05
11	P AW DMCS	11.15	0.09
12	P AW DMCS	11.80	0.22
13	P AW DMCS	12.97	0.42
14	P AW DMCS	11.93	0.60
15	P AW DMCS	13.22	1.00
16	P AW DMCS	11.01	1.99
17	P AW DMCS	11.11	2.55
18	P AW DMCS	12.84	2.85
19	P AW DMCS	11.92	4.08
20	P AW DMCS	11.02	4.89
21	P AW DMCS	13.59	9.46
22	P NAW	11.72	0.60
23	P NAW	10.66	1.00
24	P NAW	11.80	2.00
25	P NAW	11.33	4.98
26	P NAW	11.55	9.82
27	G AW DMCS	15.35	0.05
28	G AW DMCS	15.43	0.10
29	G AW DMCS	15.37	0.63
30	G AW DMCS	16.01	1.11
31	G AW DMCS	15.84	1.50
32	G AW DMCS	15.64	2.04
33	G AW DMCS	14.98	2.49
34	G AW DMCS	15.86	2.94
35	G AW DMCS	16.27	4.00
36	G AW DMCS	17.11	5.00
37	W AW DMCS	6.51	1.06
38	W AW DMCS	7.33	3.01
39	W AW DMCS	7.70	3.94
40	W AW DMCS	7.89	4.98
41	W AW DMCS	8.32	7.93
42	W AW DMCS	8.19	9.00
43	W AW DMCS	7.74	9.43
44	W AW DMCS	7.79	13.89

TABLE II

SPECIFIC SURFACE AREAS OF THE SUPPORTS

Support	*Specific surface area (m^2/g)*
Chromosorb P NAW	3.35
Chromosorb P AW	3.46
Chromosorb P AW DMCS	2.69
Chromosorb W AW DMCS	1.11
Chromosorb W AW HMDS	1.10
Chromosorb G AW DMCS	0.57

The melting point and nematic phase transition temperature for this compound is 356°K and the clearing point is 375.5°K.

The procedures used for preparing the columns and for the chromatographic determinations have been described[5]. The characteristics of the column packings are summarized in Table I. The porosity of the packings was measured with a Carlo Erba AG-65 mercury porosimeter in the pressure range 0.1–100 MPa.

The specific volume of the stationary phase compound was measured by means of a 5-cm^3 pycnometer.

The surface area of the supports was determined by the BET method from the adsorption isotherm of argon in liquid nitrogen in the pressure range 0–7.6 kPa (0–0.3 P/P_s), where P is the vapour pressure and P_s the vapour saturated pressure. The results of these determinations are summarized in Table II.

RESULTS AND DISCUSSIONS

Column packings with non-silanized supports

Fig. 1 shows the variation of the retention volume of *o*-xylene with the quantity of the stationary phase on Chromosorb P AW at 333, 349 and 358°K. The first of these temperatures lies in the solid range, 358°K in the mesophase range of the liquid

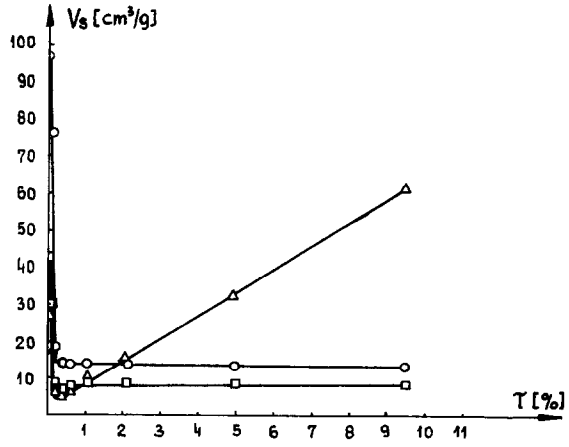

Fig. 1. Variation of the retention volume (V_s) of *o*-xylene with the amount of liquid crystalline stationary phase on Chromosorb P AW (τ). △ = 358°K; ○ = 333°K; □ = 349°K.

crystal and 349°K is the transition temperature of the additional phase found on silanized supports.

At 333°K the retention volume of *o*-xylene decreased rapidly for small amounts (up to 0.4%) of the stationary phase, and was approximately constant as the amount of the liquid crystal on the support was increased further to about 10%. A similar pattern was observed at 349°K. At 358°K the retention volume first decreased, reaching a minimum at 0.2–0.4% of stationary phase; it then increased proportionally to the amount of phase deposited on the support.

The observed rapid decrease in retention volume at small amounts (up to 0.2%) of the liquid crystal on the support and the lack of evidence of a phase transition taking place at these concentrations[5] allows us to draw some conclusions. First, adsorption of the chromatographed substance (*o*-xylene) is much greater on the non-silanized support than on the stationary phase deposited on that support. Secondly, the liquid crystal stationary phase, when deposited in small quantities on Chromosorb P AW, first covers the active adsorption centres. At this stage the support has such a great influence on the stationary phase molecules that the liquid crystalline properties are not revealed. This probably reflects the presence of a stationary phase monolayer. We can assume therefore that, in columns containing 0–0.2% of the stationary phase on the non-silanized support, adsorption on the active sites of the support, whose number decreases with increasing amount of the phase in the range 0–0.2%, is the main mechanism of retention. Hence, the retention volume is given by the relationship[6]

$$V_R = K_s (S_c - S_F)$$

where K_s is the adsorption partition coefficient, and S_c and S_F are the total surface area of the support and the surface area covered by the stationary phase, respectively. If we relate the above equation to unit weight of the support and take into account the surface area occupied by a single molecule of the stationary phase, we obtain

$$V_s = \frac{V_R}{W_s} = K_s \left[S_0 - \left(\frac{S_L N}{M_L} \right) \frac{W_L}{W_s} \right] \tag{1}$$

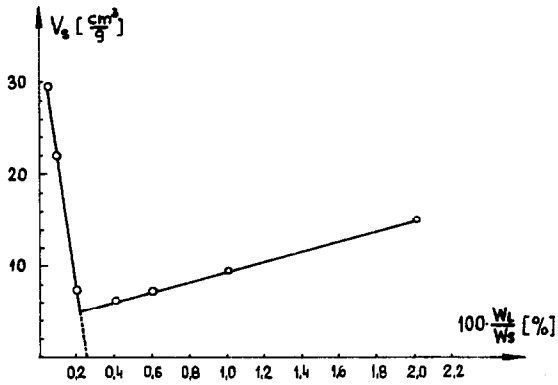

Fig. 2. Variation of the retention volume of *o*-xylene with the amount of liquid crystalline stationary phase on Chromosorb P AW at 358°K.

where S_o is the specific surface area of the support, S_L the surface area occupied by a single molecule of the phase, N the Avogadro number, M_L the molecular weight of the stationary phase, W_s the weight of the support in the column and W_L weight of the stationary phase. The relationship $V_s = f(W_L/W_s)$ for Chromosorb P AW packings is shown in Fig. 2.

If we assume that in the concentration range 0.05–0.2% eqn. 1 is fulfilled, the quantity of the liquid crystal necessary for complete coverage of the support is found by a simple extrapolation of the straight line to the ordinate axis. The value found in this way is 0.26%, corresponding to 0.75 mg liquid crystal per 1 m² of Chromosorb P AW. When the support is totally covered with a monolayer of the stationary phase, namely at 0.26% stationary phase, the following equation is fulfilled:

$$S_o = \frac{S_L N}{M_L} \cdot \frac{W_L}{W_s}$$

From this equation the surface area, S_L, occupied by a single molecule on the support is 0.806 nm². We estimated from the determined molar volume of the liquid crystal and the lengths of bonds in the molecule (available in the literature) that the liquid crystal molecule in the planar arrangement can occupy at most about 1.2 nm², while in the homeotropic arrangement it occupies at least a surface area of 0.21 nm².

From the estimated dimensions of the liquid crystal molecule given in Fig. 3 it follows that the surface area of the flat, rigid part of the molecule (hatched area in Fig. 3) is about 0.75 nm². Hence, the surface area per single stationary phase molecule calculated from experimental data (0.806 nm²) points to the possibility of a planar arrangement of the flat, rigid part of the molecule with the hydrocarbon chain bent upwards. Molecules arranged in this way may yield a monolayer bound to the support via the silanol groups of the latter. This bond with the carboxylic group of the liquid crystal is probably of the hydrogen-bonding type, and the phase molecules rigidly bound to the surface of the support will not take part in phase transitions. In this way the surface of the support is modified.

Experimental data indicate that the distribution of the first small quantities of liquid crystal on Chromosorb P NAW proceeds according to the same mechanism as on Chromosorb P AW. It is only after the formation of the monolayer is completed (0.26% stationary phase) that the process of coverage of the modified support surface commences. Usually two simplified models of distribution of a phase on a support are considered. It is either assumed that the phase is distributed on the support as a fairly uniform layer (film)[7] or that it is distributed in the form of droplets or agglomerations[8] which as the quantity of the phase increases occupy an ever greater portion

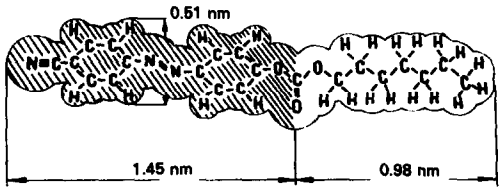

Fig. 3. The liquid crystal molecule.

of the surface area, yielding a complete layer when the quantity of the phase deposited is fairly large. In the case of the non-silanized surface of Chromosorb P we assume that, in view of the presence of the initial monolayer covering the support, further quantities of the liquid crystal will also be distributed in a uniform layer whose thickness increases gradually with the increasing quantity deposited. The variation of the retention volume with the quantity of liquid crystal at 333°K shown in Fig. 1 points to such a distribution. The constant value of the retention volume at this temperature when the quantity of stationary phase on the support exceeds 0.26% indicates that the conditions of adsorption remain unchanged, as expected if the stationary phase layer grows uniformly. However, porosity studies did not confirm this model of liquid crystal distribution.

The dependence of the pore volume on their radius for Chromosorb P AW and P NAW packings with about 1–5% of liquid crystal is presented in Fig. 4a and b, respectively. It is seen that the increase in the quantity of stationary phase from 1 to 5% produces a decrease chiefly in pores with radii greater than 1000 nm (log R = 3). The volume of smaller pores remained practically unchanged. This means that the filling of pores of non-silanized supports does not proceed uniformly over the studied range of coverage with the stationary phase, the pores with relatively large radii being filled first.

Column packings with silanized supports

The variations in the retention volume with the quantity of stationary phase deposited on silanized Chromosorb P, G and W are presented in Figs. 5, 6 and 7, respectively. As for Chromosorb P AW the relationship $V_s = f(\tau)$ is presented at three temperatures: 358, 333 and 349°K. The general character of these plots is similar for all three silanized supports, but significant differences are also observed.

At 333°K we observe on all the supports an initial increase in the retention volume with increasing quantity of the phase followed by a levelling off. This increase is observed up to about 4% of the stationary phase for Chromosorb P (Fig. 5), and to about 3 and 9% for Chromosorb G and W, respectively (Figs. 6 and 7). We conclude that the coverage of the surface area of these supports is completed at different quantities of the liquid crystal stationary phase, expressed in % (w/w).

At 358°K (mesophase) the retention volume on all three silanized Chromosorbs increased in proportion to the quantity of liquid crystal deposited over the whole range of concentrations tested.

At 349°K the retention volume initially increased linearly, and then assumed

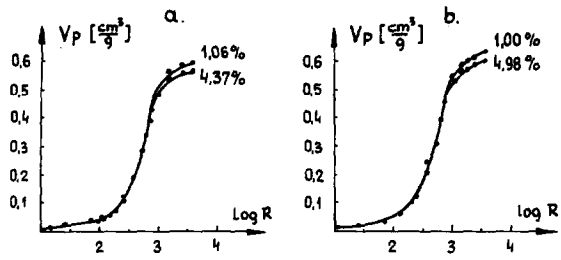

Fig. 4. The distribution of pores in column packings with about 1 and 5% stationary phase deposited on Chromosorb P AW (a) and P NAW (b) respectively. The pore radius, R, is in nm.

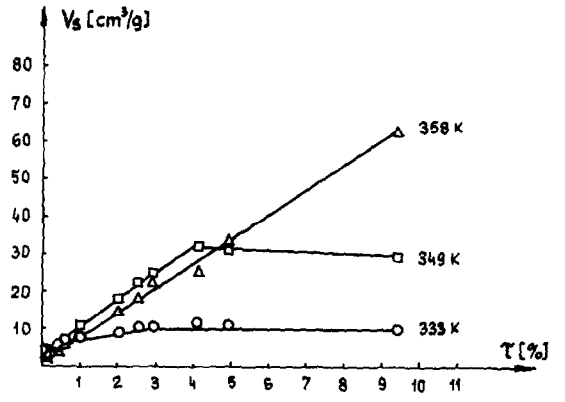

Fig. 5. Variation of the retention volume of *o*-xylene with the amount of liquid crystalline stationary phase on Chromosorb P AW DMCS.

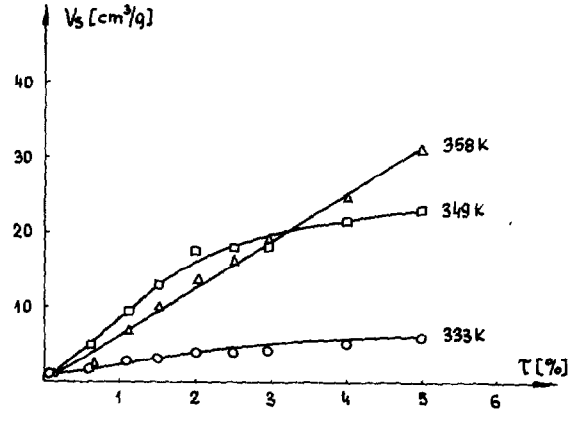

Fig. 6. Variation of the retention volume of *o*-xylene with the amount of liquid crystalline stationary phase on Chromosorb W AW DMCS.

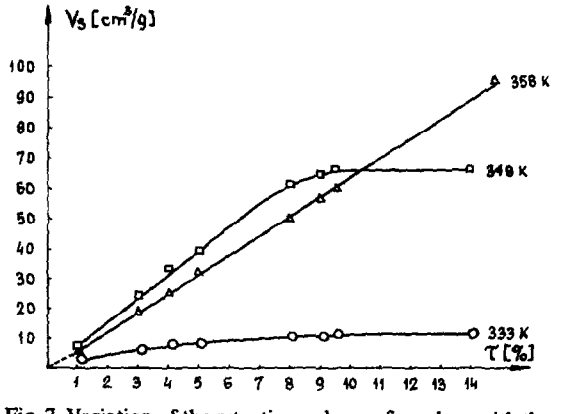

Fig. 7. Variation of the retention volume of *o*-xylene with the amount of liquid crystalline stationary phase on Chromosorb W AW DMCS.

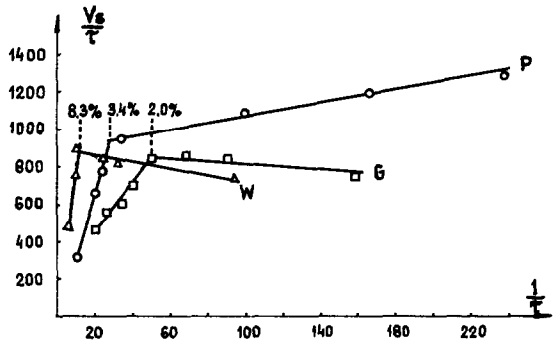

Fig. 8. Variation of the retention volume of *o*-xylene with the amount of liquid crystalline stationary phase on silanized Chromosorb P, G and W.

a constant value at greater concentrations of phase on the support. The inflection in these plots for Chromosorb G, P and W occurred at 1.5–3, 3–4 and 8–10% of the liquid crystal, respectively. Such a change in inclination of the plots means that the quantity of liquid crystal taking part in the phase transition is limited and different for each of the tested supports. The relationship $V_s = f(\tau)$ did not allow us to establish more accurately the maximum quantity of the liquid crystal that takes part in the transition which gives a stepwise increase of the retention volume with the maximum at 349°K. Good results were obtained previously[6,9] when such plots were analyzed in the form $V_s/\tau = f(1/\tau)$. Relationships of this type are presented in Fig. 8 for silanized Chromosorb P, W and G at 349°K. For each support two linear sections are found. The coverages, τ, of the support with the liquid crystal stationary phase corresponding to the points of intersection of these linear sections are 2.0, 3.4 and 8.3% for Chromosorb G, P and W, respectively. When these values are related to 1 m^2 of the support surface area, we obtain values of 35.1, 12.6 and 74.8 mg for Chromosorb G, P and W, respectively. Assuming that these quantities are distributed in an uniform layer over the whole surface area of the support, the resulting thickness of the liquid crystal layer at which the additional phase transition takes place is 11.8, 32.8 and 69.0 nm for Chromosorb P, G and W, respectively.

In order to acquire a better knowledge of the distribution of the stationary phase on the supports, we carried out investigations of the porosity of supports on which various quantities of phase were deposited. The results obtained were quite unexpected. It was found that the volume of pores with radii below 0.4 μm does not decrease as the liquid crystal stationary phase is applied, only the volume of larger pores, chiefly with radii greater than 0.8 μm, decreases. We can assume approximately that only the pores with radii greater than 0.6 μm are filled. The variation of the pore radii distribution with increasing quantity of the phase deposited on Chromosorb P and G is presented in Fig. 9. In the case of Chromosorb W the effect is less obvious since this support has practically no pores with radii below 0.2 μm. From Fig. 9, in the studied range of coverage with the stationary phase for both Chromosorb P and G, it is chiefly the pores of greater size, *i.e.*, with radii above a certain limit, in our case 0.6–0.8 μm, which are filled. This pattern can be explained if we assume that the stationary phase flows (during conditioning at 403°K) over the support surface in a layer of minimum thickness about 0.6–0.8 μm. Then all the pores of radii smaller

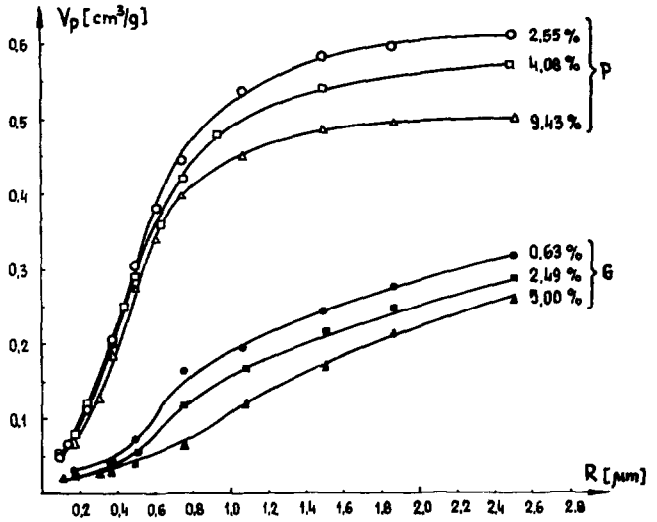

Fig. 9. Variation of the pore volume with pore radius for packings with different amounts of liquid crystalline stationary phase on silanized Chromosorb P and G.

than the thickness of this layer are sealed; the stationary phase does not enter into them but blocks the inlet channels, so a large volume of the pores remaines empty. In the porosity tests, mercury under pressure breaks through the phase film, so an unchanged proportion of pores with radii below a certain value (0.6–0.8 μm) is obtained though the amount of liquid crystal on the support is increased. It also seems possible that these small pores are sealed only when the stationary phase is in the liquid state. In the solid range the surface of the stationary phase assumes a somewhat different shape than in the case of the liquid. This may lead to the formation of slits in the film sealing the channels and in consequence to opening of the channel inlet. Pores and depressions of radii greater than the thickness of the film are partially filled and their volume decreases proportionally.

The elimination of a considerable portion of the pores from the chromatographic process, accompanied by a significant reduction in the mass exchange surface area, is a consequence of the described distribution of the stationary phase on the surface of the silanized supports. This reduction in surface area depends on the support used, *i.e.*, on the contribution of pores with radii smaller than the expected thickness of the stationary phase layer (0.6–0.8 μm) to the total pore volume and surface area of the support.

The liquid crystal layer 0.6–0.8 μm thick seals the pores of diameter 1.2–1.6 μm; as a result the surface area participating in the mass exchange is reduced to the greatest extent for Chromosorb P, to a lesser degree for Chromosorb G and to the smallest extent for Chromosorb W. Thus the layers formed on different supports do not have different thicknesses, as could be expected from the varying quantities of the phase undergoing transition at 349°K, but are of similar thickness on all supports whose surface areas are reduced by various degrees. Assuming that 2, 3.4 and 8.3% of the stationary phase is distributed on Chromosorb G, P and W, respectively, in a layer about 0.6 μm thick, we calculated the stationary phase–carrier gas contact

surface areas to be 0.03, 0.05 and 0.13 m^2 per 1 g of support, respectively. This presents a significant reduction of surface area as compared with the specific surface area of the supports themselves. It follows that the mass transfer surface area afforded by the supports used is taken advantage of only to a very small degree. A particularly significant decrease in the mass transfer surface area takes place in the case of silanized Chromosorb P. A fairly good utilization of the support surface area is achieved in the cases of supports with large pore diameters.

CONCLUSIONS

This study has shown the significant effect of the support surface area on the properties of chromatographic column packings incorporating liquid crystal stationary phases. The liquid crystals comprising electronegative elements or groups may participate in hydrogen bonds with the silanol surface groups, as observed on the surfaces of non-silanized supports. The liquid crystal molecules bound in this way reside on the support surface in the form of a monolayer which does not undergo phase transitions. The formation of such a monolayer is not a sufficient condition for a further uniform distribution of the liquid crystal on the surface of the support. When the liquid crystal was deposited in greater quantities it accumulated in pores of large diameters. We did not observe the filling of pores with radii smaller than 1 μm.

It should be noted that in analytical applications the effect of the support is much greater when liquid crystal stationary phases are used than with non-liquid crystal ones. Besides, the efficiency and selectivity of columns with liquid crystal stationary phases are largely affected by mass transfer resistances. Good selectivity is achieved when the quantity of the stationary phase applied is small and the mass transfer surface area is large. The highest selectivity on silanized Chromosorb G, P and W has been obtained for columns containing 2.5, 3 and 8% (w/w) of the liquid crystal, respectively, *i.e.*, corresponding to a layer thickness of about 0.6 μm.

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REFERENCES

1 Z. Witkiewicz and S. Popiel, *J. Chromatogr.*, 154 (1978) 60.
2 Z. Witkiewicz, Z. Suprynowicz and R. Dabrowski, *J. Chromatogr.*, 175 (1979) 37.
3 Z. P. Vetrova, O. A. Vyakhirev, N. T. Karabanov, G. G. Maidatschenko and J. A. Jashin, *Chromatographia*, 8 (1975) 643.
4 Z. P. Vetrova, N. T. Karabanov and J. A. Jashin, *Chromatographia*, 10 (1977) 341.
5 W. Marciniak and Z. Witkiewicz, *J. Chromatogr.*, 207 (1981) 333.
6 K. Naito and S. Takei, *J. Chromatogr.*, 190 (1980) 21.
7 J. G. Giddings, *Anal. Chem.*, 34 (1962) 458.
8 J. A. Jönsson and L. Mathiasson, *J. Chromatogr.*, 179 (1979) 1.
9 J. Rayss, Z. Witkiewicz, A. Waksmundzki and R. Dabrowski, *J. Chromatogr.*, 188 (1980) 107.