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PHASE TRANSITIONS OF 4-CYANO-4'-*n*-ALKOXYFORMYLOXYAZOBENZENES ON SILANIZED SUPPORTS

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SUMMARY

The phase transitions of 4-cyano-4'-*n*-alkoxyformyloxyazobenzene liquid crystals deposited on silanized supports have been investigated. It was found that the transitions depend on the heat conditioning treatment of the column packings and not on the type of substance chromatographed. Heat conditioning was found to have a strong effect on the structure assumed by the liquid crystal on the support. An additional phase transition of the liquid crystal on silanized supports is observed only in two cases. Some differences in results were observed depending on whether the liquid crystal phase transitions were studied by chromatographic or calorimetric procedures.

INTRODUCTION

The interactions between a stationary phases and the support upon which it is deposited may affect the retention of chromatographed substances. In the case of liquid crystal stationary phases, the interaction with the support may result in a change in the structure of the liquid crystal. The support may affect the selectivity of liquid crystal stationary phases¹⁻⁴ and the heat of solution of the chromatographed substances^{1,5}. Depending on the kind of support used, the liquid crystal mesophase range may be extended, phase transitions may disappear and new transitions may occur^{1-4,6}.

In earlier work we studied the effect of the support surface on the chromatographic properties of 4-cyano-4'-*n*-heptyloxyformyloxyazobenzene (C7)^{7,8}. The results of these investigations made it possible to determine the distribution of the liquid crystal on the surface of the support for different amounts of phase deposited different supports (Chromosorb NAW, AW and AW DMCS).

In the case of columns packed with silanized supports an additional phase transition of the liquid crystal was detected at 7°K below its melting point^{7,8}. We decided therefore to investigate in the present work whether this phenomenon depends not only on the nature of the support but also on the conditioning of the columns and on the substance chromatographed. It was also our intention to determine whether the additional phase transition occurs with other 4-cyano-4'-*n*-alkoxy-

TABLE I

PHASE TRANSITION TEMPERATURES OF TESTED 4-CYANO-4'-*n*-ALKOXYFORMYLOXY-AZOBENZENES

K = Solid; N = nematic; S = smectic; I = isotropic.

Compound	Alkyl (<i>R</i>)	Phase transition temperatures ($^{\circ}\text{K}$)			
		K-N	K-S	S-N	N-I or S-I
C3	-C ₃ H ₇	378			397.5
C5	-C ₅ H ₁₁	355			384
C6	-C ₆ H ₁₃	357			378.5
C7	-C ₇ H ₁₅	356			375.5
C8	-C ₈ H ₁₇	371			374.5
C9	-C ₉ H ₁₉		348	351	371
C10	-C ₁₀ H ₂₁		357.5	361	370
C11	-C ₁₁ H ₂₃		360	366.5	369
C12	-C ₁₂ H ₂₅		362		370

formyloxyazobenzenes containing 3-12 carbons (C3-C12) in the alkyl chain. We expected to obtain some information about the nature of the observed phase transitions from calorimetric studies of the liquid crystal transitions taking place on the supports.

EXPERIMENTAL

The procedure used for the chromatographic investigations and the method of calculating the retention parameters were described in an earlier paper⁷.

By the calorimetric method we determined the enthalpies and phase transition temperatures of the liquid crystals deposited in various amounts on the supports. The measurements were made using a Du Pont differential scanning calorimeter with a registering device. Aluminium trioxide was used as the reference. The masses of the samples were about 15 mg. The measurements were made during heating at a rate of 1 $^{\circ}\text{K}/\text{min}$.

The phase transition temperatures of the liquid crystals are summarized in Table I and the characteristics of the investigated columns in Table II.

TABLE II

CHARACTERISTICS OF COLUMN PACKINGS

Column No.	Phase	Chromosorb	Amount of stationary phase on support (%)	Weight of column packing (g)
1	C7	W AW DMCS	9.0	8.19
2	C3	G AW DMCS	3.05	18.33
3	C5	G AW DMCS	3.0	17.3
4	C6	G AW DMCS	2.96	17.06
5	C8	G AW DMCS	2.86	17.8
6	C9	G AW DMCS	3.0	17.2
7	C10	G AW DMCS	2.92	16.91
8	C11	G AW DMCS	3.08	17.08
9	C12	G AW DMCS	3.02	16.97

RESULTS AND DISCUSSION

Chromatographic tests

The results of earlier studies indicated that the additional transition of the liquid crystal C7 is closely related to the way in which it is distributed on the surface of a silanized support^{7,8}. It was of interest therefore to check whether the final distribution of the liquid crystal on the support takes place during the course of deposition from the solvent or whether heat conditioning of the column plays a rôle. Several experiments were carried out in which the columns were tested after deposition of the liquid crystal on the support, but without heat conditioning; the columns were then conditioned at 403°K and tested again. The variations in the retention time with temperature observed in these experiments are presented in Fig. 1 for a column filled with Chromosorb W AW DMCS upon which 9% of the C7 phase had been deposited.

It is seen from Fig. 1 that the shape of the plot of retention vs. column temperature depends on whether the column was or was not heat conditioned before the test. Similar results were obtained in other experiments, allowing us to conclude that the structural form of the C7 stationary phase undergoing transition at 349°K is established chiefly during heat conditioning of the column. If the column is conditioned at a temperature about 30°K higher than the clearing point, the viscosity and surface tension of the liquid crystalline stationary phase are lowered significantly. This creates a better contact with the silanized surface which by its nature is non-wettable. The liquid crystal phase expands (flows) to cover greater areas of the support around the initial spots occupied directly after deposition from the solvent. This results in two effects as observed in Fig. 1. First, there is increased retention in the solid range due to greater adsorption of the chromatographed substance, which in turn is due to the growth (in the course of heating) of the surface area of the liquid crystal stationary phase and its more effective distribution on the support. Secondly, there is an increase in the maximum retention volume at 349°K. This suggests that

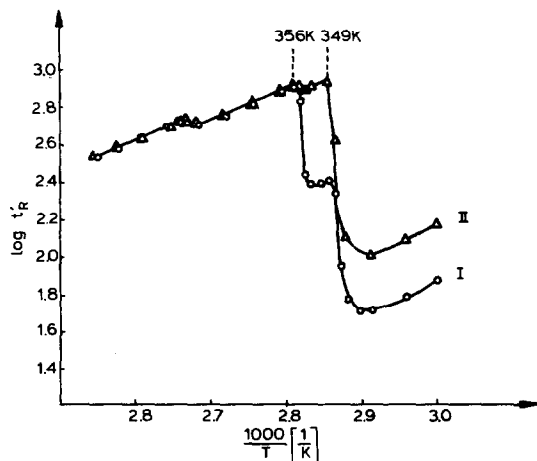


Fig. 1. Variation in *o*-xylene retention time with temperature on column I (9% phase C7 deposited on Chromosorb W AW DMCS). I, Before column heating; II, after heating at 403°K.

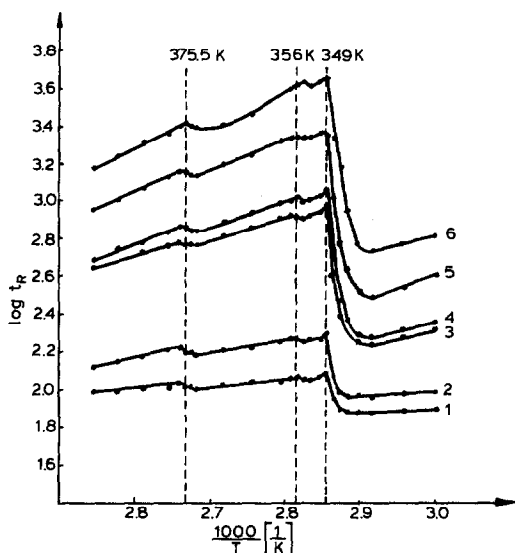


Fig. 2. Variation in retention time of various substances with temperature on column 1. Curves: 1, cyclohexane; 2, benzene; 3, *o*-xylene; 4, *n*-propylbenzene; 5, 1,4-diethylbenzene; 6, cyanobenzene.

during heat conditioning, or more precisely, during the cooling which follows heating, a certain part of the stationary phase probably assumes a crystalline structure different from that of the remaining phase. By implication, small proportion of this structural form is present during deposition from the solvent. However, the structure type generated under the influence of the support is formed chiefly during the heating of the column.

In the earlier tests^{7,8} xylene isomers, compounds having very similar physicochemical properties, were used as the test substances. Hence, it was of interest to determine whether the phase transitions of the C7 liquid crystal on silanized supports are also observed in the chromatography of substances with more differentiated physicochemical properties. This was studied using columns with Chromosorb W AW DMCS on which 9% of the C7 phase had been deposited. Several examples of the dependences of the retention time on the column temperature are presented in Fig. 2 for substances with different structures and polarities varying from zero (benzene, cyclohexane) to 4.1 D (cyanobenzene). The corresponding phase transition temperatures characteristics of the stationary phase-support systems observed in these tests did not differ by more than 1°K from the corresponding temperatures observed in the case of xylene as solute.

We also wished to determine whether the additional phase transition observed for the liquid crystal C7 on silanized surfaces takes place also in the case of other 4-cyano-4'-*n*-alkoxyformylloxazobenzene liquid crystals. Liquid crystals differing in the terminal alkyl group (from C3 to C12, except C4) were tested. Fig. 3 shows the dependence of the retention volume on temperature for packings with these liquid crystals, together with the phase transition temperatures. The additional transition was observed also for the C9 phase. Apart from the increased retention corresponding to the melting of this liquid crystal at 348°K, another increase in the retention

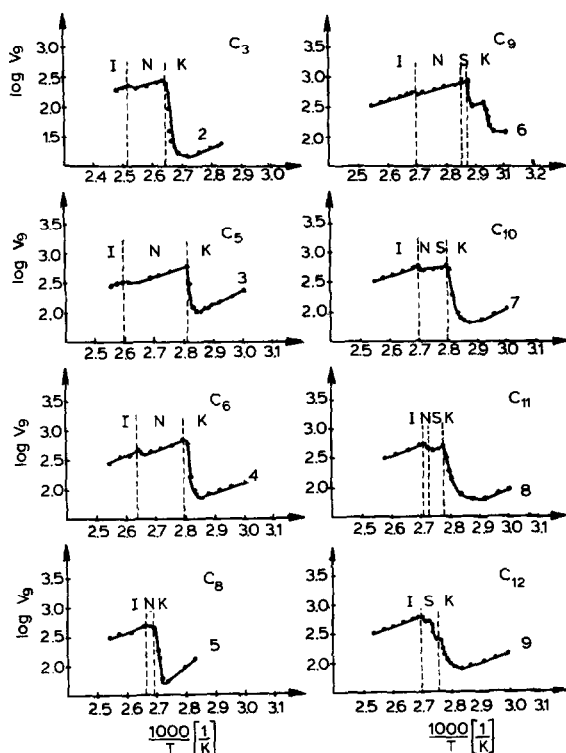


Fig. 3. Variation in *o*-xylene retention volume with temperature on different columns. The columns and the liquid crystals are indicated.

volume occurred with a maximum at 342°K, *i.e.*, 6°K below the melting point as determined by the thermo-optical method. This indicates that the C7 and C9 phases have similar properties and similar interactions with the surfaces of silanized supports.

Calorimetric tests

The calorimetric tests were carried out to determine the energetic effects of the phase transitions observed in the chromatographic tests, especially for packings with various amounts of the C7 liquid crystal deposited on silanized supports. The molar enthalpies of the phase transitions of this liquid crystal at 349 and 356°K are summarized in Table III.

The phase transition of C7 at 349°K was found to take place in all packings with silanized supports. The transition temperatures determined calorimetrically were in agreement within $\pm 1^\circ\text{K}$ with those determined in chromatographic experiments. The principal difference between the two sets of results was that there was no correlation between the retention increments and the thermal effects of the transitions occurring at 349 and 356°K. The thermal effects of the transition at 356°K was in all cases the greater, even when the chromatographic tests revealed only the transition at 349°K, which was the case with all the packings when the quantity of the liquid

TABLE III

CALORIMETRICALLY MEASURED ENTHALPIES OF PHASE TRANSITIONS OF THE C7 LIQUID CRYSTAL

Support	Amount of liquid crystal (%)	Enthalpies (kJ/mol)		I + II
		At 349°K I	At 356°K II	
Chromosorb	0.60	2.43	24.33	26.76
P AW DMCS	1.00	2.89	25.30	28.19
	1.99	5.37	25.20	30.57
	2.85	5.63	21.26	26.89
	4.08	7.52	23.08	30.60
	4.89	6.83	22.12	28.95
Chromosorb	0.63	3.48	23.17	26.65
G AW DMCS	2.49	9.49	18.69	28.18
	4.00	10.95	20.99	31.94
	5.00	11.31	17.15	28.46
Chromosorb	3.01	10.22	19.47	29.69
W AW DMCS	9.00	9.76	18.02	27.78
	9.43	6.08	22.20	28.28
	13.89	5.25	23.63	28.88

crystal allowed coverage below a certain limit, *i.e.*, 2.0, 3.4 and 8.3% for Chromosorb G, P and W, respectively.

Chromatographic tests showed that these coverages involve the maximum quantities of the liquid crystal that melt on the silanized supports at 349°K. It is necessary therefore to explain which effect is responsible for the enthalpy measured in the calorimetric tests of these packings at 356°K. The explanation must be sought in the physicochemical properties of the liquid crystals. In this context, the effect of the terminal groups of the liquid crystal molecule on the physicochemical properties would seem important. It has been found that the clearing point of the 4-cyano-4'-*n*-alkoxyformyloxyazobenzenes decreases as the length of the alkyl chain increases (Fig. 4). Probably the high melting and clearing points observed for compounds with short alkyl chains are due to the formation of linear dimers via dipole interactions⁹. The latter interactions, connected with the presence of the cyano group, are greatest in liquid crystals with short molecules. As the length of the hydrocarbon chain, and hence the whole molecule of the liquid crystal, becomes longer the dispersive interactions and their contribution to the total energy of interaction between the liquid crystal molecules also increase. An increase in the dispersive interactions inhibits the translation and the formation of the smectic phase in compounds with alkyl groups longer than C₉. Thus the contribution of the dipole interaction forces to the total interaction of the molecules decreases with increasing alkyl chain length.

The C7 and C9 liquid crystals are intermediate between those compounds with prevailing namatogenic interactions of the cyano group and those in which the smectogenic effect of the alkyl chain prevails. This provides a partial explanation of why the additional phase transition occurs only in these two liquid crystals. The phase transition occurring at 6 °K (for C9) or 7°K (for C7) below the melting points in the

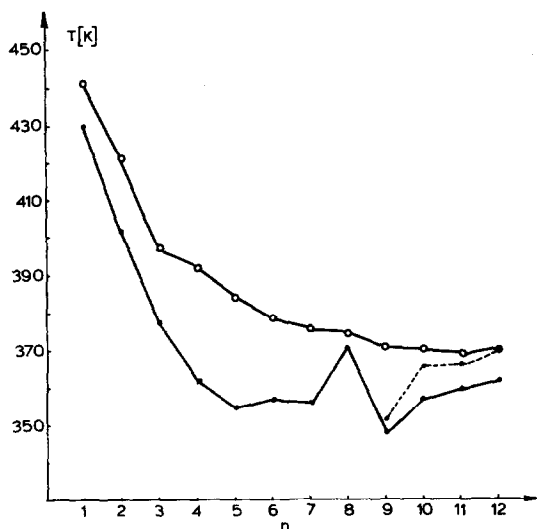


Fig. 4. Temperatures of the clearing (○—○), melting (●—●) and smectic-nematic phase transitions (---) as function of alkyl chain length in 4-cyano-4'-*n*-alkoxyformyloxyazobenzene molecules.

absence of the support is probably related to the specific properties of these two liquid crystals. The absence of this phenomenon in the case of compound C8 becomes obvious if we consider the observed alternation of properties in homologous series, *i.e.*, neighbouring compounds in the series with even or odd numbers of carbon atoms exhibit similar properties⁹. The alternation in properties of series of liquid crystals is also true of their properties as stationary phases in gas chromatography¹⁰.

Despite the similarity in properties of the C7 and C9 liquid crystals a difference occurs between their mesophases. In the case of C7 only the nematic mesophase was found to occur, while in the case of compound C9 both the nematic and smectic phases were observed. This means that during cooling the C9 liquid crystal is a smectic and C7 is a nematic in the vicinity of the freezing point, as determined thermo-optically. Despite this a considerable structural similarity seems possible. This may be due to the existence in the C7 liquid crystal nematic phase of cibotactic groups of smectic structure. Such groups appear in the nematic phase, during cooling of certain liquid crystals, at temperatures preceding the nematic-to-smectic transition point. These groups consist of several dozen to several hundred molecules and their volume increases as the temperature is lowered to the nematic-to-smectic transition point. The presence of cibotactic groups has also been detected in liquid crystals in which the smectic phase did not occur¹¹. One can suppose that this is the case with the C7 phase. The occurrence of the smectic phase in the successive homologue with an odd number of carbon atoms in the alkyl chain, C9, confirms this supposition. Besides, compound C9 is an A-type smectic (confirmed thermo-optically) and thus a mesophase whose structure is closest to the nematic one. It is possible therefore that the C7 liquid crystal nematic phase has in the vicinity of the freezing point a structure resembling very closely that of the C9 smectic.

For packings comprising the C7 liquid crystalline phase on silanized supports,

as in the case of compound C9, it is probable that the transition at 349°K involves several or several dozen layers of smectic ordering. The structure of these layers may be different from that of the bulk liquid crystal, *e.g.*, a different packing of the molecules or different coordination in the smectic layers. If we assume that the smectic layers of C9 and the cibotactic groups of compound C7 have a dimeric structure, then the structure of the layer close to the surface of the support may be monomeric. In this layer adjacent to the methylated surface of the silanized support, a homeotropic arrangement of the liquid crystal molecules is favoured with the aliphatic chain oriented towards the support surface. If we assume that the whole surface of the support is covered with molecules arranged in this way, then in the cooling step this arrangement may compete with the dimeric structure, resulting in the formation at a certain distance from the surface of the support of a monomeric mesophase structure differing from that in the bulk phase. This structure is transformed into the dimeric one at the melting point as determined thermo-optically. The corresponding transition was not recorded in the chromatographic tests, which may be justified by the fact that the chromatographic tests allow us to detect only those phase transitions which are accompanied by distinct structural changes. Apparently the differences in the structure of the C7 liquid crystal layer close to the support surface below and above 356°K are insignificant and therefore cannot be recorded chromatographically. However, they have been revealed in the form of a second endothermic peak (at 356°K) by the calorimetric procedure. This model of the melting process of the C7 liquid crystalline phase explains the appearance of the endothermic peak at 356°K for packings for which chromatographic tests revealed solely the transition at 349°K. The enthalpy recorded for at 356°K is related to the change in the structure of the layer next to the surface layer of the liquid crystal on the support. This is a transition of the monomeric structure into the dimeric one and is characteristic of the given liquid crystal. It can therefore be assumed that for certain small quantities of the C7 and C9 stationary phases melting proceeds with the formation of a new mesomorphic phase, as was observed in the cases of re-entrant phases.

CONCLUSIONS

The phase transition observed in the present work below the melting point of the liquid crystals are due to the formation under the influence of the support surface of a liquid crystal layer whose structure differs from that of the bulk liquid crystal. This effect is independent of the chromatographed substance but depends on the nature and quantity of the liquid crystal on the support and is characteristic of the liquid crystal-support system. These results demonstrate the importance of taking account of the interactions of the stationary phase with the support even when the latter has been silanized.

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