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Studies on Induced Smectic Phases (II)

Transition Enthalpies, X-ray Patterns and Layer Spacings of Orthogonal Phases of Binary Mixtures of Nematogens with Contrasting Dielectric Anisotropies¹⁾

Binary mixtures of two nematogens, 4,4'-di-n-heptyl-azobenzene with 4-n-pentyl-4'-cyano biphenyl were studied by optical, calorimetric and X-ray measurements. At a given concentration induced phases with a sequence S_A , S_B , S_E were detected, the properties of which were discussed.

Binäre Mischungen von zwei Nematogenen, 4,4'-Di-n-heptylazobenzenen mit 4-n-Pentyl-4'-cyanobiphenyl, wurden mit optischen, kalorimetrischen und röntgenographischen Methoden untersucht. Bei bestimmten Konzentrationen wurden induzierte Phasen der Sequenz S_A , S_B und S_E nachgewiesen. Die strukturellen und thermischen Eigenschaften dieser Phasen werden berichtet.

1. Introduction

Transition enthalpies of binary mixtures of smectogens and cholesterogens indicated a deviation from the ideal behaviour if one of the components has a polar para-substituent. In these systems induced smectic phases were observed. The estimated A-B interaction energies of induced smectic A phases were approx. 1.5–2.5 kJ per mole⁻¹ (SZABON, JANOSSY). Now, further studies in a system of 4,4'-di-n-heptyl-azobenzene (7 AB) with 4-n-pentyl-4'-cyanobiphenyl (5 CB) were performed by different methods to characterize the induced phases and the responsible interactions (SZABON, PILZ). The studies on the above system were a part of the examinations of binary mixtures of (2*n*-1)-AB with *m*-CB homologues (*n* = 1–5, *m* = 5–8) chosen as components for mixtures of zero or negative dielectric anisotropy $\Delta\epsilon$, on the one hand with high positive $\Delta\epsilon$ on the other (SZABON, J.).

2. Experimental

7 AB was synthesized by M. Pinter. The purity was not less than 99.8% by DSC (SIKLOS, SZABON). 5 CB was kindly provided by BDH in pure form (purity about 99.9%). Mixtures were prepared in small quantities (100 mg) using analytical balance. Perfect mixing was obtained by a hotstage together with ultrasonic mixing in the isotropic state. No detectable degradation of the samples was found during the measurements.

Kofler's contact method was applied to establish the type of the phase diagram. DSC measurements were used to construct the detailed form of the diagram. The different

¹⁾ Part II of this series. Part I: SZABON, J., JANOSSY, I., Part III: SZABON, J., PILZ, W., Part IV: SZABON, J.

induced smectic phases were assigned both by texture analysis applying the contact method (RICHTER) and by X-ray diffraction methods. The lengths of the molecules, L_{7AB} and L_{5CB} , were measured in their most stretched-out all-trans conformation using kalott models.

Transitional heats were measured using Perkin-Elmer DSC-2B. The data were processed by on-line (PET) microcomputer.

3. Results

3.1. Phase diagram and transition enthalpies

By contact method under the polarizing microscope five mesomorphic areas were distinguishable, separated by heterogeneous two-phase regions (Fig. 1). The two nematic phases separated by the smectic ones were different in texture (schlieren

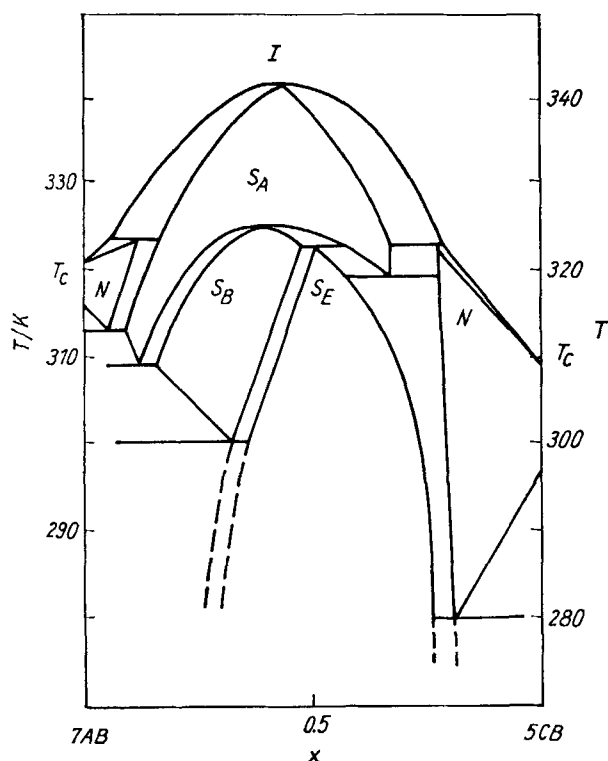


Fig. 1. Isobaric phase diagram for binary mixtures 7AB and 5CB

and homeotropic). The three induced smectic phases could be assigned to S_A , S_B , and S_E according to their different texture patterns (focal-conic, mosaic and striped mosaic). The central part of the isobaric phase diagram around 320 K as well as the other two-phase areas could be accurately determined by the DSC-measurements of mixtures with different concentrations. The supercooling of the S_E phase was found to be significant.

Transition enthalpies measured by DSC are shown in Figure 2 as a function of the mole fraction. Their maxima are: S_E at $x = 0.5$; S_B around $x = 0.33$; S_A : broad maximum between $x = 0.3-0.5$.

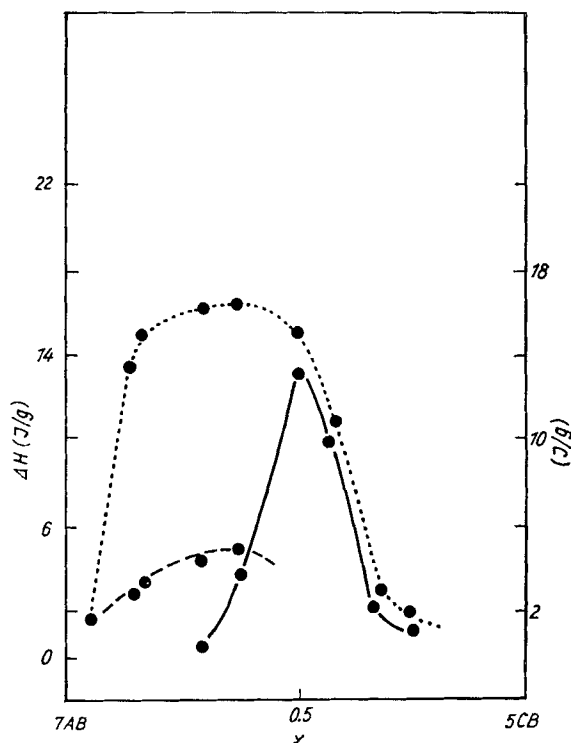


Fig. 2. Enthalpies of the transition. $S_B \leftrightarrow S_A$ (S_B): solid line; $S_B \leftrightarrow S_A'$: dashed line; $S_A \leftrightarrow I$: dotted line

3.2. Layer spacings

Layer spacings (d) measured at different concentrations as a function of the temperature do not show an essential temperature dependence in the smectic phases. Therefore, it is possible to compare the d values in different phase types of different mixtures with the lengths of the molecules, L_{7AB} and L_{5CB} , respectively. In Figure 3 the values of $T = 305$ K were shown. At the left side of the diagram, up to a mole fraction $x = 0.5$, the values fulfill the rule of additivity

$$d = x_{7AB}L_{7AB} + x_{5CB}L_{5CB}. \quad (1)$$

The rule is found in all binary systems of liquid crystals in which structures with orthogonally arranged molecules in the layers are mixed (DIELE et al.).

At the right side of the diagram positive deviations from the rule were observed the values of which are increasing with increasing concentration of the polar component. This behaviour observed in other systems, too (ENGELN et al.) was explained by an equilibrium of monomers and dimers which is shifted into direction of the dimers with increasing concentration of the polar substance (DIELE et al.; CLADIS et al.). Hence a kind of "bi-layer" structure follows. In the case of the pure compound (5 CB) the maximum of the diffuse inner ring in the nematic phase was used to calculate a d value. A relation $d = 1.3L_{5CB}$ is deduced (see also LEADBETTER et al.). It should be emphasized that no hints of a tilted arrangement of the building units in the nematic phase exist according to our investigations of oriented samples.

3.3. Structures of the induced smectic phases

The diffraction patterns taken with a Guinier equipment at the concentrations $x = 0.40$, $x = 0.50$, and $x = 0.70$ as the function of the temperature prove the assignment of the phases to the types S_E , S_B , and S_A , respectively.

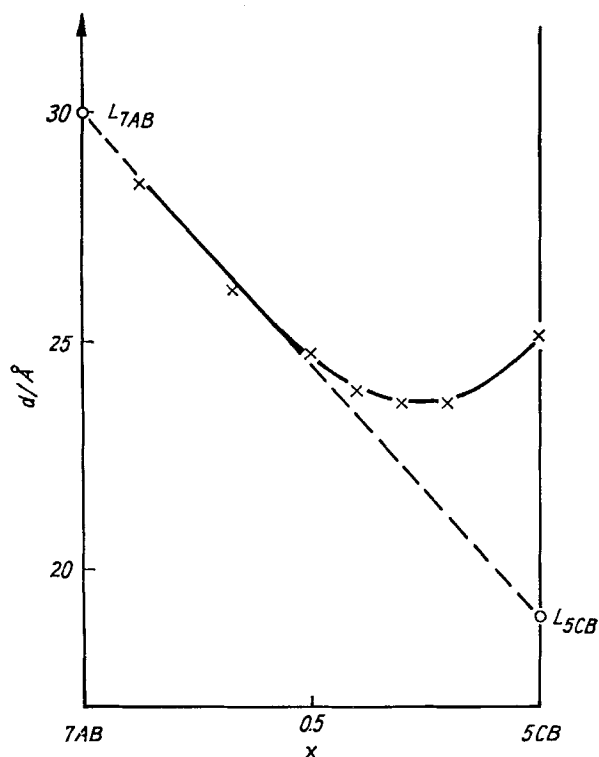


Fig. 3. Layer spacings at 305 K (solid line); layer spacings calculated (dashed line) according equ. 1

The existence of one outer reflection in the patterns of the S_B phase points to a hexagonal packing of the molecules (Fig. 4a).

The patterns of the S_E phases (Fig. 4b) exhibit a relatively high number of reflections demonstrating a well ordered packing within the smectic layers (Tab. 1). It proves that the incorporation of different molecules in one and the same layer does not destroy the structural order.

The reflections are compatible with an orthorhombic unit cell with a herring-bone packing in the a - b plane. The type of packing is generated by a glide mirror plane parallel to the a or b lattice vector, which can be derived by the extinction rule. Table 2 shows the calculated lattice constants of the three mixtures. The structure is in agreement with the S_E structures of other substances.

At a mixture with $x = 0.70$ well oriented samples were obtained by slow cooling from the isotropic state within a magnetic field of about 2 Tesla (Fig. 5). The spot like character of the pattern (the first one, which is observed in a mixture) proves the high degree of order in this mixed phase. It established the chosen indexing. Additional reflections resulting from a two components system and irregularities concerning the packing of adjacent layers because of the different molecular lengths could not be detected.



Fig. 4. X-ray patterns of the S_B (a) and of the S_E phase (b) of a mixture $x = 0.40$

Table 1

Observed and calculated Bragg-angles of the reflections at the pattern of a mixture $x = 0.5$

| $\theta_{\text{obs.}}$ | hkl | $\theta_{\text{calc.}}$ |
|------------------------|-------|-------------------------|
| 1.79 | 001 | 1.79 |
| 9.93 | 110 | 9.93 |
| 10.06 | 111 | 10.09 |
| 10.96 | 200 | 10.96 |
| 11.13 | 201 | 11.10 |
| 13.80 | 210 | 13.79 |
| 14.04 | 211 | 13.91 |
| 17.68 | 120 | 17.64 |
| 18.69 | 310 | 18.63 |
| 20.24 | 220 | 20.17 |
| 23.96 | 320 | 23.90 |

Table 2

Calculated lattice constants

| | $x = 0.33$ | $x = 0.50$ | $x = 0.70$ |
|----------------|------------|------------|------------|
| $a/\text{\AA}$ | 8.22 | 8.10 | 8.01 |
| $b/\text{\AA}$ | 5.37 | 5.35 | 5.35 |
| $c/\text{\AA}$ | 26.2 | 24.7 | 23.7 |

Diffuse scattering at the (001) lattice node perpendicular to the $\langle 001 \rangle$ row in the reciprocal lattice proves the orthogonal arrangement of the building units. This diffuse scattering can be explained by small translational motions of strings of molecules in direction of the lattice vector c .

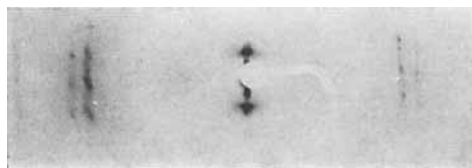


Fig. 5. Pattern of an oriented sample ($x = 0.70$) at $T = 300 \text{ K}$

Summary

The studies were limited to a system of binary mixtures of nematogens with minimal lateral dipole moments and contrasting dielectric anisotropies: 7AB is an apolar and 5CB is a polar compound. The electron withdrawing $-\text{CN}$ group plays a dual role probably in enhancing the lateral cohesive and terminal repulsive interactions between nearest neighbours (SZABON, JANOSSY). Phase inductions are yielded: resulting S_A phase at a broad concentration range, the S_B phase with a maximum of thermal stability at 2:1 of $x_{7AB}:x_{5CB}$, and a S_E phase as found to be most stable at 1:1 mole ratio.

These ratios can be explained on the base of the structures of the S_B and S_E phases, which demand three or two molecules in the unit cell, respectively.

The charge transfer interaction responsible for this phase induction is weak (SZABON, JANOSSY; SZABON, PILZ), no molecular compound is formed. The sequence of phases is $S_E, S_B, S_A (N)$ at a concentration given. No tilted phases were detected (in contra-

diction to DAVE et al.). The corresponding structures exhibit a hexagonal arrangement in the S_B and an orthorhombic cell with a herring-bone type of packing in the S_E phase.

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References

- CLADIS, P. E., GUILLON, D., BOUCHET, F. R., FINN, P. L.: Phys. Rev. **A23**, 2594 (1981)
DAVE, J. S., VORA, R. A.: in *Liqu. Cryst. Plast Cryst*, Vol. 1, p. 153 (Eds GRAY, G. W. and WINDSOR, E., Chichester 1974)
DIELE, S., NASTA, L., SACKMANN, H.: *Krist. u. Technik* **12**, 1063 (1977)
DIELE, S., BAUMEISTER, U., DEMUS, D.: *Z. Chem.* **21**, 27 (1981)
ENGELN, B., HEPPKE, G., HOPF, R., SCHNEIDER, F.: *Ann. Phys.* **3**, 403 (1978)
LEADBETTER, A. J., RICHARDSON, R. M., COLLING, C. N.: *J. Phys.* **36**, C1—37 (1975)
RICHTER, L.: personal communication
SIKLOS, L., SZABON, J.: in: *Adv. Liqu. Cryst. Res. Appl.* (Ed. L. BATA) Oxford 1980, p. 237
SZABON, J., JANOSSY, I.: in: *Adv. Liqu. Cryst. Res. Appl.* p. 229 (Ed. L. BATA) Oxford 1980
SZABON, J., PILZ, W.: to be published
SZABON, J.: in: *4th Liqu. Cryst. Conf. Soc. Countries/Tbilissi* 1981, to be published

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