

Intermediate Phases in Binary Liquid Crystalline Systems

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The diagrams of state of three binary systems have been studied. One of these shows appearance of intermediate phases of the type N and S_A , while in the other two diagrams, either N or S_A phase, as intermediate one, are observed. The explanation for their appearance is provided. The smectic C and smectic I phases of HOAB remain restricted on its respective side and do not show any miscibility with smectic C phases of HBBA and HBOA.

THE occurrence of electron donor acceptor (EDA) interactions in liquid crystals was provided in homologous series of 4,4'-bis-[n-alkyl-amino]-biphenyls¹. Induced nematic and smectic phases were found in mixtures of potentially liquid crystalline donors and acceptors². The charge transfer bands in the visible region have been observed in some liquid crystalline mixed phases³. The formation of induced smectic phases is said to occur whenever there is an enhancement in the liquid crystalline-isotropic transition temperatures⁴. Further, in some cases, a change in colour in the region of mixed phases in contact preparations⁵ was observed. In case of intermediate phases, neither the enhancement in the liquid crystalline-isotropic transition temperatures nor any charge transfer interaction was observed. This paper reports the diagrams of state between HOAB as one component, and BBEA, HBBA and HBOA as the other ones, in which the intermediate phases have been observed.

Experimental

Materials: The following substances, with their known polymorphy were used in this work.

(i) 4,4'-Bis-n-hexadecyloxy-azoxybenzene (HOAB); $C_{16}H_{33}O-C_6H_4-N=N-C_6H_4-OC_{16}H_{33}$ (Found \downarrow
Cr[†]. 89.2 S_I 91.4 S_C 115.7 Is. Requires⁵ Cr. 89.5 S_B 91.1 S_C 115.5 Is).

The low temperature smectic phase, which was earlier classified as S_B , has now been classified as smectic I phase. This classification depends on the textural and the miscibility studies⁶.

(ii) N-[4-n-Butyloxy-benzylidene]-4'-ethylaniline (BBEA); $C_4H_9O-C_6H_4-CH=N-C_6H_4-C_2H_5$ (Found Cr. 37.8 S_G 50.0 N 65.0 Is. Requires Cr. 38.7 S_G 50.5 N 64.8 Is).

(iii) N-[4-n-Heptyloxy-benzylidene]-4'-n-butylaniline (HBBA); $C_7H_{15}O-C_6H_4-CH=N-C_6H_4-C_4H_9$ (Found Cr. 32.6 S_G 63.2 S_C 65.0 S_A 74.2 N 76.7 Is. Requires Cr. 31.5 S_G 62.5 S_C 63.6 S_A 73.0 N 75.5 Is).

(iv) N-[4-n-Heptyloxy-benzylidene]-4'-n-octylaniline (HBOA); $C_7H_{15}O-C_6H_4-CH=N-C_6H_4-C_8H_{17}$ (Found Cr. 48.0 S_G 52.7 S_B 68.7 S_C 70.3 S_A 83.0 Is. Requires Cr. 48.0 S_G 52.5-53.0 S_B 68.4-69.0 S_C 70.3 S_A 82.7-83.0 Is).

The transition temperatures and classification of the phases BBEA, HBBA and HBOA are the same as assigned in the earlier reports^{7,8}, except for the low temperature phase represented as smectic H, which has now been agreed to be represented as smectic G phase⁹.

Microscopic study: The miscibility investigations on HOAB as one component, and BBEA, HBBA or HBOA as the other one were carried out on a polarizing microscope fitted with a microheating stage by Koffler's contact method¹⁰.

Results and Discussion

The binary systems were so chosen that one liquid crystal shows low temperature smectic I modification (HOAB), and the other possesses smectic B or smectic G or both the phases (BBEA, HBBA, HBOA). The results of different binary systems are as follows.

System 1 (HOAB/BBEA): The diagram of state of this binary system is provided in Fig. 1. S_C and S_I modifications of HOAB and N and S_G phases of BBEA remain restricted to their respective sides. S_A and N appear as intermediate phases. S_A phase appears at 97.5° from isotropic liquid and solidifies by 81.3°. Similarly, nematic phase appears at 91.3° on cooling the preparation and solidifies at 75.2°. In between 75.2 and 69.5°, the system

† Abbreviations: Cr = crystalline solid state; S_A, S_B, \dots, S_I = smectic modifications of the type, A, B, \dots , I, respectively, N = nematic phase; Is = isotropic liquid state; cl p. = clearing point; m.p. = melting point; and tr₁, tr₂, \dots = first, second \dots transitions in liquid crystalline state.

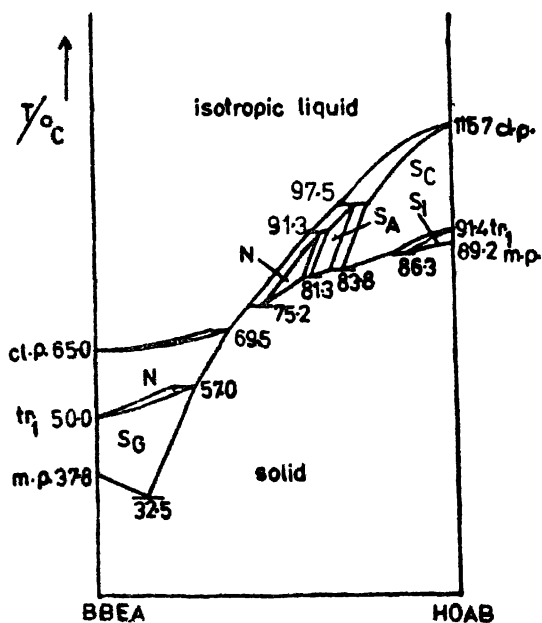


Fig. 1. Binary diagram of state of system HOAB and BBEA.

solidifies directly from isotropic liquid. The eutectic in this binary system is found at 32.5°. Nematic phase on the left hand side does not mix with intermediate nematic phase and has been separated by the solid region.

System 2 (HOAB/HBBA) : The diagram of state of this binary system is given in Fig. 2. The miscibility between S_C phases in both the components is not observed. S_C/S_I heterogeneous region shows a maximum at 94.4°. An intermediate phase of the type S_A appears from 98.9 to 81.5°

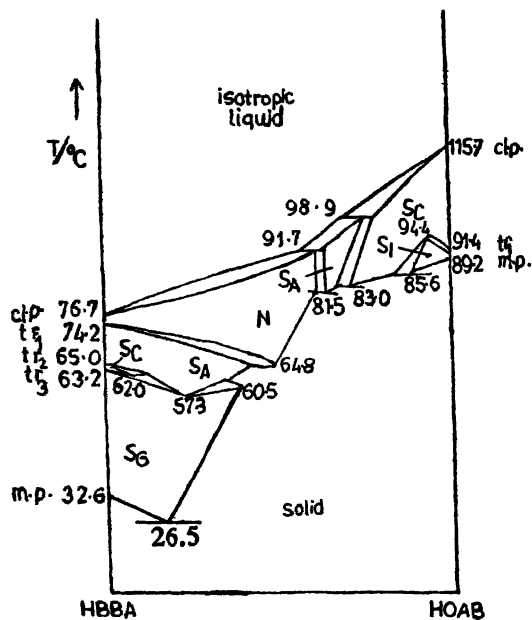


Fig. 2. Binary diagram of state of system HOAB and HBBA.

which does not extend itself to provide any miscibility with the S_A phase of HBBA. Eutectic is obtained at 26.5°.

System 3 (HOAB/HBOA) : The smectic C phases of HOAB and HBOA as well as S_I phase of HOAB give similar results as system 2. Smectic A phase extends itself and possesses the largest area in this diagram of state. Although S_B and S_G modifications extend themselves, but are suppressed by the presence of existence of S_A phase. Nematic phase appears as an intermediate phase at 89.5° through a three-phase reaction, isotropic liquid + $S_A \leftrightarrow N$ as shown in Fig. 3. The heterogeneous region of $N - S_A$ has a minimum at 78.2°.

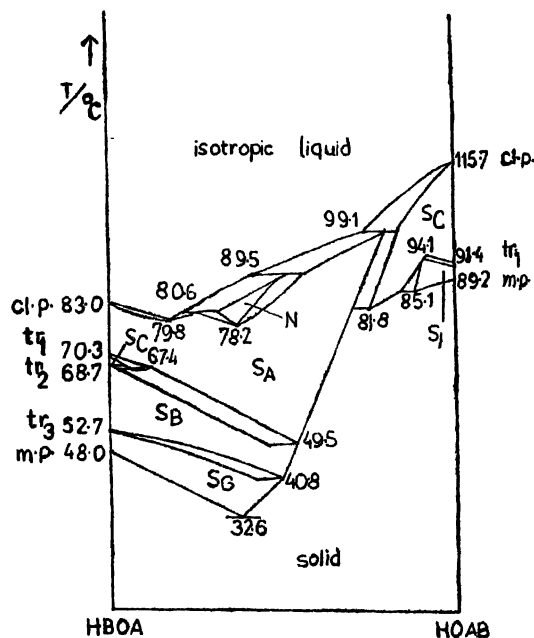


Fig. 3. Binary diagram of state of system HOAB and HBOA.

Thus in all these systems, HOAB was mixed with different substances of the homologous series of N -[4- n -alkoxy-benzylidene]-4'- n -alkylaniline. The substances of this homologous series possess S_C , S_B and S_G phases in addition to N and S_A phases in some of their derivatives. The smectic B and smectic G phases of this homologous series and smectic I phase of HOAB remain restricted on their respective sides. In all the systems, except system 1, a maximum in the heterogeneous region of S_C and S_I phases have been observed. The intermediate phases of the type N and S_A have been observed in systems 3 and 2, respectively, while in system 1, both nematic as well as smectic A appear as intermediate phases. The existence of intermediate nematic phase in systems 1 and 3 can be interpreted due to the existence of nematic phase in heptyl and lower homologous of the series N -[4- n -heptyloxy-benzylidene]-4'- n -alkylaniline. The appearance of intermediate S_A phase in these systems can be explained from the existence of S_A phase in other

homologous of *N*-[4-(4-*n*-alkyloxy-benzylidene)-4'-*n*-alkylaniline]. The intermediate phases of N and S_A types do not show any miscibility with N and S_A modifications present on the left hand side of these diagrams of state. It may be possible that the crystallization front from pure HOAB does not allow the intermediate phases to extend their regions. Further, HOAB does not show much undercooling. S_A phase also does not appear in other homologous series of 4,4'-bis-*n*-alkadecyloxy-azoxybenzene.

An intermediate S_C modification, which is tilted to the layers, has been observed in the binary system of 4,4'-bis-[*n*-octadecyl-amino]-biphenyl and *n*-amyl-4-[4'-*n*-dodecyloxy-benzylidene-amino]-cinnamate¹. S_B phase also appears as an intermediate phase in the binary systems between *n*-amyl-4-[4'-*n*-dodecyloxy-benzylidene-amino]-cinnamate and 4,4'-bis-[*n*-decyl-amino]-biphenyl and between C₉/C₁₈ and C₁₀/C₁₈ homologous of 4,4'-bis-[*n*-alkyl-amino]-biphenyl and 4,4'-bis-[*n*-octadecyl-amino]-biphenyl², respectively.

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