

Miscibility Studies of some Liquid Crystalline Substances with Hexadecyloxyazobenzene

N. K. SHARMA* and R. K. BAMEZAI

Liquid Crystal Group, Department of Chemistry, University of Jammu, Jammu-180 004

Manuscript received 9 July 1991, accepted 20 September 1991

The diagrams of state have been studied for some binary liquid crystal mixtures. Each of the systems studied contains hexadecyloxyazobenzene (HOAB) as one component while the other one is hexyloxybenzylideneaminoazobenzene (HBAAB), heptyloxybenzylidene heptylaniline (HBHA) and methoxybenzylidene-aminoethylcinnamate (MBAEC). All the phases in these systems remain confined to their respective sides. On the basis of miscibility studies with HOAB, smectic B phase in HBAAB, HBHA and MBAEC is established.

In the homologous series 4,4'-bis-(n-alkylamino)-biphenyl¹ and terephthalylidene-bis(4-n-butyl)aniline², a new low temperature modification named as smectic I was observed. The low temperature modification of 4,4'-bis-n-hexadecyloxyazobenzene (HOAB) was classified as smectic B modification³. But the miscibility studies of HOAB with 4-n-pentyl (4'-n-dodecyloxybenzylideneamino)cinnamate (PDOBAC) showed uninterrupted miscibility of smectic C and also the low temperature modifications of both the components showed an uninterrupted miscibility. As the low temperature modification of PDOBAC was found to be smectic I, hence the low temperature phase of HOAB was reclassified as smectic I phase⁴.

In the present paper, miscibility studies of HOAB and some liquid crystalline substances which possess smectic B phase are presented.

Experimental

The substances used and their polymorphism are (i) 4,4'-bis-n-hexadecyloxyazobenzene (HOAB) $C_{16}H_{33}O-C_6H_4-N=N-C_6H_4-OC_{16}H_{33}$, Cr 89.2



SI 91.4 Sc 115.7 Is; (ii) 4-(4'-n-hexyloxybenzylidene-amino)azobenzene (HBAAB) $C_6H_{13}O-C_6H_4-CH=N-C_6H_4-N=N-C_6H_5$, Cr 89.0 S_B 124.9 S_A 145.0 N 172.7 Is; (iii) N-(4-n-heptyloxybenzylidene)-4'-n-heptylaniline (HBHA) $C_7H_{15}O-C_6H_4-CH=N-C_6H_4-C_7H_{15}$, Cr 33.2 S_G 50.0 S_B 65.4 S_C 70.3 S_A 82.8 N 84.0 Is and (iv) 4-(4'-methoxybenzylidene-amino)ethylcinnamate (MBAEC) $CH_3O-C_6H_4-CH=N-C_6H_4-CH=CH-COOC_2H_5$, Cr 106.8 (S_B 91.3) S_A 117.4 N 139.9 Is. The above experimentally determined values are in good agreement with the reported values^{5,6,7}. The binary diagrams of state were studied first by contact method followed by determination of transition temperature of their singular mixtures made at specific concentrations.

Results and Discussion

Transition temperatures and the phase sequences were systematically investigated in three binary systems, in which one of the components was HOAB and the other was chosen with smectic B modification. The binary systems HOAB/HBAAB, HOAB/HBHA and HOAB/MBAEC were investigated.

Fig. 1 shows singular concentration diagram of state between HOAB/HBAAB. The smectic A phase of pure HBAAB extends even upto 70% of HOAB

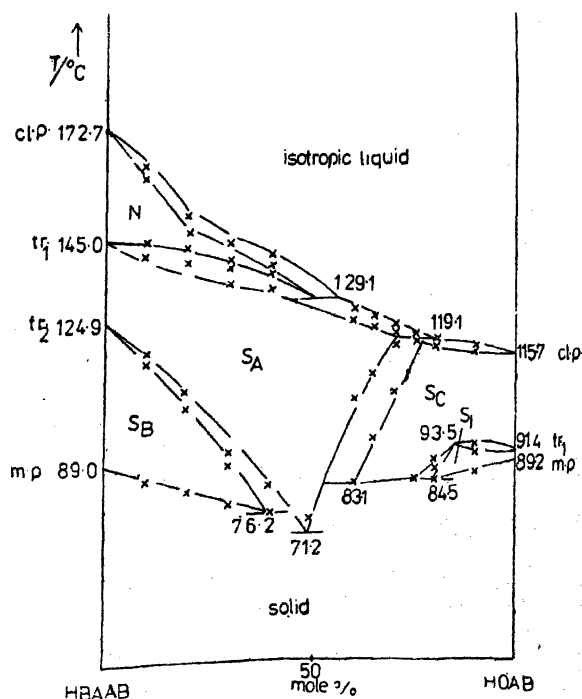


Fig. 1. Diagram of state between HOAB and HBAAB.

where it emerges from isotropic liquid which later crystallises into the eutectic at 71.2° . The nematic, smectic B, smectic C and smectic I remain restricted to their sides. Smectic A phase of HBHA extends to higher concentration region of HOAB as shown in Fig. 2. The other smectic phases remain confined to their narrower regions which simultaneously

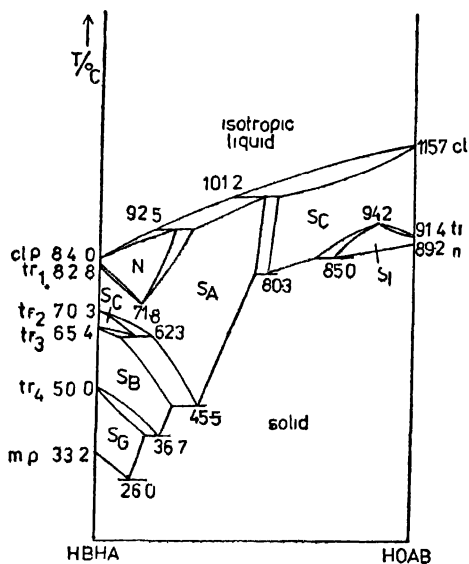


Fig. 2. Diagram of state between HOAB and HBHA.

change into crystalline solid. In Fig. 3, the trimorph class of pure substance, i.e. MBAEC shows monotropic smectic B phase. When mixed with HOAB, it shows two regions: stable and monotropic. The nematic phase from stable region passes into monotropic region and crystallises at 92° . The S_A phase also forms stable region (117°) and extends to high concentration region of HOAB. The monotropic part of S_B passes into solid state at 81.8° . These monotropic areas existing only on cooling are irreversible and hence are represented by dotted lines.

A survey of these systems shows that in Figs. 1 and 2, a maximum in the heterogenous region of smectic C and smectic I phases is observed while a minimum in N/ S_A region is observed in Fig. 2. A heterogenous region of immiscibility is also observed between S_A and S_C phases in all these systems. These do not run parallel to the temperature axis but are slightly bent and often lie at the higher concentrations of one of the components, i.e. HOAB. These immiscibility gaps are also distinctly reproducible in contact preparations as well. The steric and energetic reasons are responsible for the phase regions starting at respective pure components to extend only over restricted concentrations in binary systems which is the case in Fig. 2.

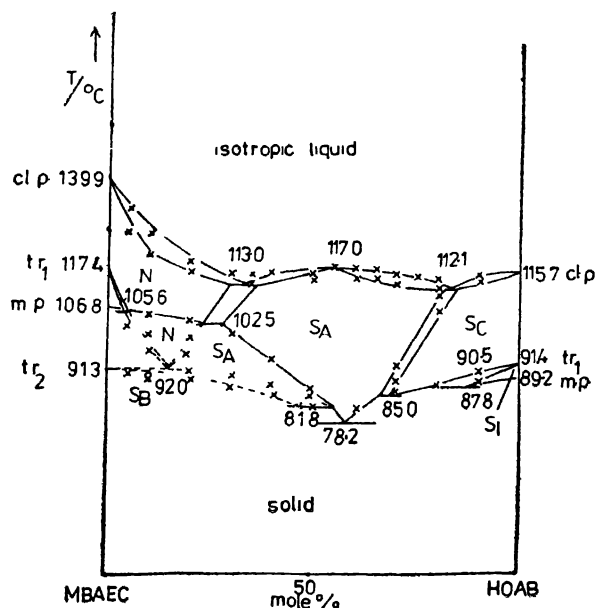


Fig. 3. Diagram of state between HOAB and MBAEC.

The immiscibility gaps have also been observed between tilted B (now smectic I) and orthogonal B phases⁶. The tilted smectic B phase was later found to be smectic I phase due to its complete miscibility with smectic I phase of nonyl- and decyl-homologues of the terephthalylidene-bis-alkylanilines. However, in our investigations, smectic B phase, as shown by its textural studies is orthogonal and hence its immiscibility with smectic I phase of HOAB could be one of the reasons for their appearance in a smaller region. On the basis of miscibility investigations, the liquid crystals HBAAB, HBHA and MBAEC thus possess orthogonal smectic B phase.

The marbled textures were shown for nematic phase while small focal conics textures of smectic A appear in all these systems. The smectic B were also fan shaped and were recognisable by diminished number of discontinuities. The textures of smectic C and smectic I were those of schlieren and divided fan shaped type. The mosaic textures were visible in smectic G phase.

Acknowledgement

One of the authors (R.K.B.) is thankful to C.S.I.R., New Delhi, for Pool Officership.

References

1. N. K. SHARMA, W. WEISSFLOG, L. RICHTER, S. DIELE, B. WALTHER, H. SACKMANN and D. DEMUS. "Advances in Liquid Crystal Research and Applications", ed. L. BATA, Pergamon, Oxford, 1980, Vol. 1, p. 3.

2. L. RICHTER, N. K. SHARMA, R. SEUBATZ, D. DEMUS and H. SACKMANN, *Mol. Cryst. Liq Cryst*, 1982, **80**, 195.
3. D. DEMUS, H. KÖNIG, D. MARZOTOKO and R. RURAŃSKI, *Mol. Cryst Liq Cryst*, 1978, **23**, 207.
4. N. K. SHARMA, Dissertation, Martin Luther University, 1979
5. D. DEMUS, H. DEMUS and H. ZASCHKE, "Flüssige Kristalle in Tabellen", VEB Deutscher Verlag für Grundstoffindustrie, Leipzig, 1976
6. N. K. SHARMA, *Indian J. Chem., Sect. A*, 1981, **21**, 4