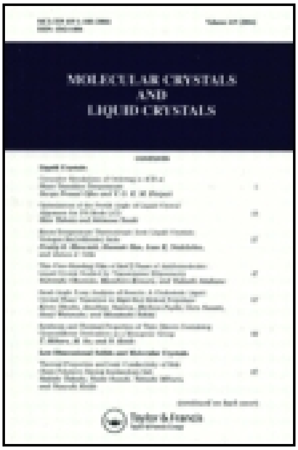


Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Binary Liquid Crystal Systems with Two Eutectics

N. K. Sharma [a b] , I. Müller [a] , R. Wingen [a] , H. R. Dübal [a] , C. Escher [a] & D. Ohlendorf [a]

[a] HOECHST AG, APh, 6230, Frankfurt 80, F. R. G.

[b] Dept. of Chemistry, Univ. of Jammu, Jammu Tawi, 180 004, India

Version of record first published: 17 Oct 2011.

To cite this article: N. K. Sharma , I. Müller , R. Wingen , H. R. Dübal , C. Escher & D. Ohlendorf (1987): Binary Liquid Crystal Systems with Two Eutectics, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 151:1, 225-231

To link to this article: http://dx.doi.org/10.1080/00268948708075333

Mol. Cryst. Liq. Cryst., 1987, Vol. 151, pp. 225-231
Photocopying permitted by license only

Printed in the United States of America

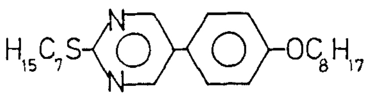
BINARY LIQUID CRYSTAL SYSTEMS WITH TWO EUTECTICS

N. K. SHARMA*, I. MÜLLER, R. WINGEN, H. R. DÜBAL,
C. ESCHER, D. OHLENDORF
HOECHST AG, APh, 6230 Frankfurt 80, F. R. G.

Abstract Some binary liquid crystal mixtures based on phenyl-pyrimidine derivatives are investigated. Some of these derivatives are new and were found to have SmC or SmC* phases. They exhibit unusual binary phase diagrams like the existence of two eutectics and induced smectic A and smectic C phases. In some cases the melting point at intermediate concentrations is considerably higher than that of the two single substances. This indicates that a new compound is formed at about equal concentrations of the two substances. A possible explanation, the formation of an EDA complex, is discussed.

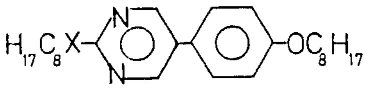
NEW SMECTIC C COMPOUNDS

A number of new homologues of 5-phenyl-pyrimidin derivatives[1] has been synthesized and were found to exhibit various smectic phases. The following examples have been subsequently investigated in binary mixtures (K = crystalline, S = smectic phase with the index giving the smectic modification):



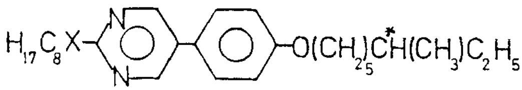
K 39 (S_G 34) S_C 51 S_A 75 I (I)

* On leave from Dept. of Chemistry, Univ. of Jammu, Jammu Tawi-180 004, India



x = S: K 51 (S_G 40) S_C 55 S_A 75 I (II)

x = O: K 76 (S_C 69) S_A 99 I (III)

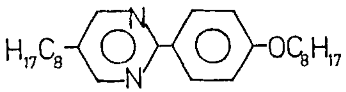


x = S: K 43 S_C^* 55 S_A 60 I (IV)

x = O: K 73 S_C^* 78 S_A 86 I (V)

BINARY MIXTURES

Binary phase diagrams of each of the compounds (I) to (V) with the well-known 2-phenyl-pyrimidine derivative [2]



K 29 S_C 56 S_A 62 N 69 I

were established. For this purpose we used three different techniques:

(a) contact preparation microscopic
(b) fixed concentration ratios texture
(c) DSC-measurements

The results as shown in Figs. 1 to 4 show the occurrence of the following phenomena:

The phase diagrams of (I) and (II) with (A) (Fig. 1) each exhibit two eutectic points and a distinct maximum of the melting curve inbetween. The S_C-phases are severely suppressed whereas the stability of the S_A-phase is increased at intermediate concentrations (induced S_A-phase).

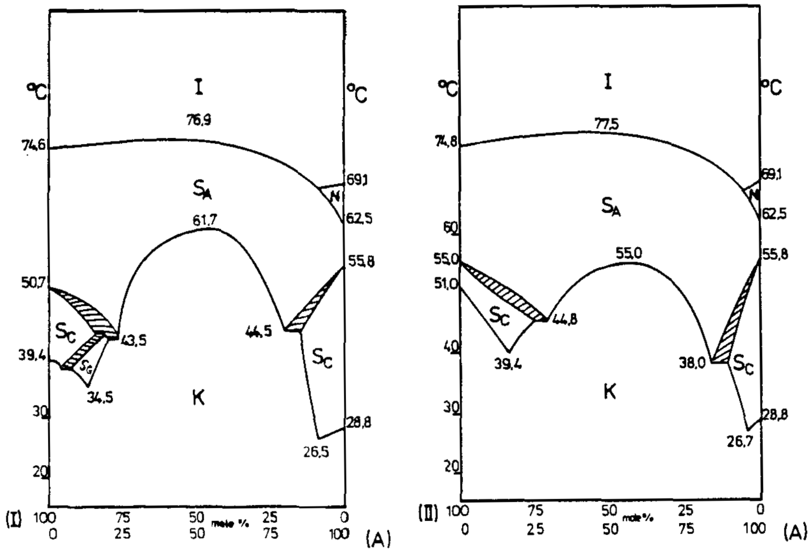


FIG. 1 The increase in melting point at intermediate concentrations in the binary phase diagrams of compounds (A) and (I) and (A) and (II) is much more drastical than similar effects reported in the literature 3 - 5. The hatched areas are two-phase-regions.

An exchange of the sulphur atom by an oxygen atom in compound (II) leads to the phase diagram shown in Fig. 2. Though not as clearly visible as in Fig. 1 analogous phenomena seem to occur. Their presence is partly suppressed by the large temperature difference in melting point and in clearing point of the two compounds (III) and (A).

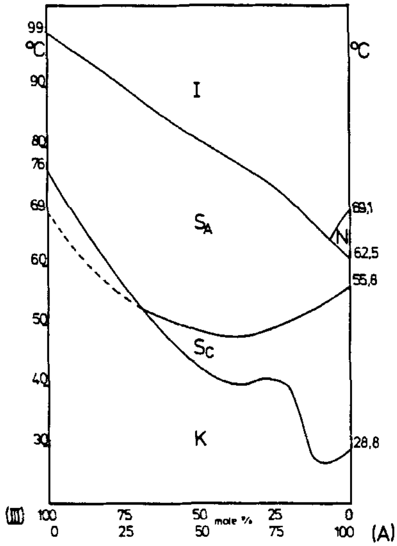


FIG. 2 Binary phase diagram of (A) and (III).

The picture looks quite different, however, when (A) is blended with compounds (IV) and (V) (cf. Figs. 3, 4). Here we have the clear existence of one eutectic point and both S_A and S_C phases are well miscible. Actually the phase diagram of (A) and (IV) (Fig. 3) demonstrates the seemingly very rare case of an induced S_C-(or S_C^*-)phase.

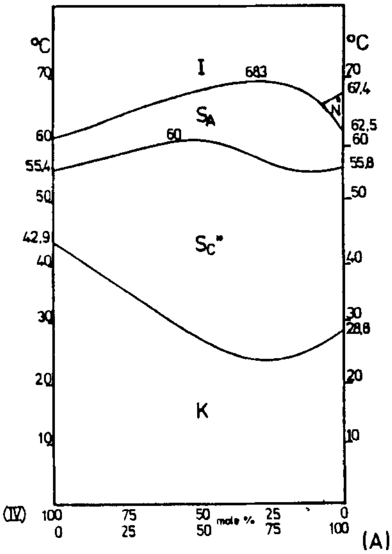


FIG. 3. Binary phase diagram of (A) and (V)

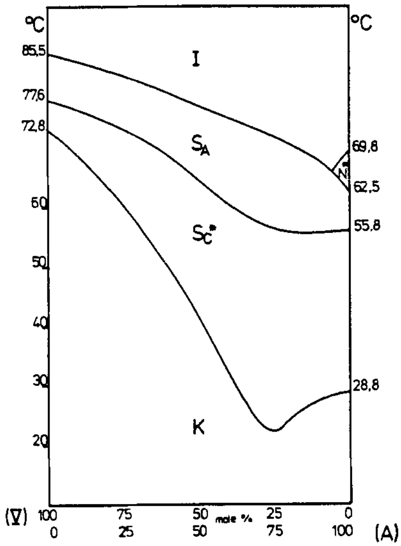


FIG. 4. Binary phase diagram of (A) and (V)

DISCUSSION

The existence of two eutectics 3 - 5 or of an induced S_A--phase 4 - 7 in a binary liquid crystal system is not new. But it seems to have never been observed in mixtures without any terminally polar molecules. Hence the effects cannot be due to an association of terminal parts of molecules.

Another possibility is the formation of an Electron Donator Acceptor (EDA) Complex 4 - 6 as a new compound. To obtain a rough idea whether such a complex formation is conceivable one can look at the various mesomeric structures which can be drawn for molecules of type (A) on the one hand and for those of type (I) and (II) on the other. When we restrict ourselves to those mesomeric structures which have only two charge centres we find double as many structures with an additional electron in the aromatic ring system for (I) and (II) as compared to (A). Equivalently one can say that in (I) and (II) both the sulphur and oxygen atom exert a + M-effect whereas in (A) only the oxygen atom can give electrons to the ring system. The resulting increased average electron density in the ring system of (I) and (II) as compared to (A) is consistent with the finding that the refractive index in the isotropic phase of compound (II) is about 0.02 larger than that in the isotropic phase of (A).

Therefore it is conceivable that molecules (I) or (II) act as electron donators and molecules (A) as electron acceptor in an EDA complex. Further investigations have to be made, though, in order to confirm our assumption. One such investigation is finding out the existence of a Charge Transfer (CT) Band. As our mixtures were seemingly colourless such a band should be in the UV range.

The strikingly different behaviour of the branched 'analogues' to (II) and (III), namely (IV) and (V) can partly be explained by the fact that steric intermolecular hindrance might favour liquid crystal behaviour as compared to crystallization. This effect is frequently observed in the field of liquid crystals and manifests itself in a depression of the melting point of homologues with branched alkyl chains as compared to those with straight chains. Yet, a full understanding of the processes leading to the phase diagram as shown in Fig. 3 with induced S_C^* and S_A phases requires a more detailed investigation. The same is true for the phenomenon as shown in Figs. 1 and 2. The occurrence of various different crystalline modifications may also be of importance.

The phenyl-pyrimidines presented in this article represent a convenient system to study unusual and interesting phenomena which might occur on blending various pure compounds.

REFERENCES

1. D. Demus and H. Zaschke, Flüssige Kristalle in Tabellen II (VEB Deutscher Verlag für Grundstoffindustrie, Leipzig, 1984), pp. 376-378.
2. D. Demus and H. Zaschke, Flüssige Kristalle in Tabellen, (VEB Deutscher Verlag für Grundstoffindustrie, Leipzig, 1974), # 4164
3. G. Pelzl, S. Diele, A. Wiegeleben and D. Demus, Mol. Cryst. Liq. Cryst. 64, 163 (1981)
4. D. Demus, G. Pelzl, N. K. Sharma and W. Weissflog, Mol. Cryst. Liq. Cryst. 76, 241 (1981).
5. W. H. de Jeu, L. Longa and D. Demus, J. Chem. Phys. 84, 6410 (1984)
6. N. K. Sharma, G. Pelzl, D. Demus and W. Weissflog, Z. Phys. Chem. 261, 579 (1980)
7. F. Schneider and N. K. Sharma, Z. Naturforsch. 36 a, 62 (1981)