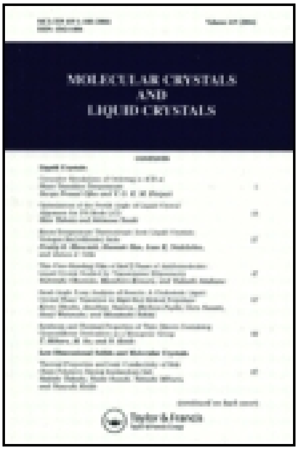

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Liquid Crystalline Behaviour of Mixtures of Mesogens and a Non-Mesogen in Binary Systems

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Liquid Crystalline Behaviour of Mixtures of Mesogens and a Non-Mesogen in Binary Systems

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We have studied four binary systems comprising of four mesogenic components viz., 4-nitrophenyl-4$^{|}$-n-alkoxy benzoates (where n-alkoxy group is n-butoxy, n-hexyloxy, n-octyloxy and n-decyloxy) and a non-mesogenic component namely., 4-n-decyloxy-4$^{|}$-1-(s)-methyl propoxy azobenzene.

A wide variety of mixed mesomorphic properties are observed in these mixtures. The properties of these systems are discussed on the basis of phase diagrams.

Keywords: Mixtures, non-mesogen; smectogen; binary systems; non linearity; polymesomorph

INTRODUCTION

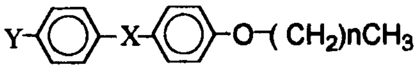
The liquid crystal state is accepted as an intermediate state of existence, hence, some nonmesogenic substances could have the potential to exhibit mesormorphic behaviour. But the mesophase does not appear because the temperature of the transition from an amorphous liquid to the mesophase lies below the normal melting point. Such substances in their binary mixtures with a liquid crystalline substance or even a non liquid crystalline substance can give rise to "mixed liquid crystal" formation over a range of temperature and composition.[1]

Most of the binary mixtures do not under go any change in their mesomorphic textures[2], though a few have been reported giving rise to different textures. Emergence of mesophase, increase or decrease of the mixed mesomorphic range, thermal stabilities and the study of the factors which influence the modification have received more attention.[3] We have reported mixtures were a higher ordered smectic phase emerges from mixtures of nematogens[2] and a lower order nematic phase emerges from mixture of a smectogen [4] and a non mesogen. We have also reported binary systems of structurally similar and dissimilar mesogens and nonmesogens.[5] However binary mixtures with chiral components are less explored.

Keeping this in view, we report here four binary systems consisting of structurally dissimilar mesogens and a non mesogen with a chiral terminal group and the study of their effect on mixed mesomorphism, arising due to the differences in structural characteristics of these components.

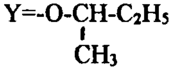
The binary mixtures are composed of a non mesomorphic chiral azo derivative (A) namely, 4-n-decyloxyphenylazo-4'-1-(s)-methyl propoxy benzene and esters (B_1-B_4) viz. 4-nitrophenyl-4'-n-alkoxybenzoates.

The components have the following general structural formula



where

A : DPAB ; n=9 X= -N=N-;



$Y=-O-\underset{CH_3}{CH}-C_2H_5$

Transition temperature °C : K 70 I

B_1 : NPBB ; n=3 X=-COO-; $Y=-NO_2$

Transition temperature °C : K 55 I

B_2 : NPHB ; n=5 X=-COO-; $Y=-NO_2$

Transition temperature °C : K (52) N 68 I

B_3 : NPOB ; n=7 X=-COO-; $Y=-NO_2$

Transition temperature °C : K 49 Sc 62 N 66 I

B_4 : NPDB ; n=9 X=-COO-; $Y=-NO_2$

Transition temperature °C : K 60 Sc 78 I

The binary systems studied are

(I) DPAB + NPBB (II) DPAB + NPHB
(III) DPAB + NPOB (IV) DPAB + NPDB.

EXPERIMENTAL

All the chemicals used were of Fluka, B.D.H or Aldrich grade. 4-1-(s)-methyl propoxy aniline[6, 7], 4-hydroxyphenylazo-4-1-(s)-methyl propoxy benzene[8] and 4-nitrophenyl-4^{1}-n-alkoxybenzoates[5] were synthesised by reported methods. 4-n-decyloxyphenylazo -4-1- (s) methyl propoxybenzene was prepared by alkylating the azo compound with n-decyl bromide. The final compounds were recrystallized from ethanol and their elemental analysis were carried out in Coleman USA

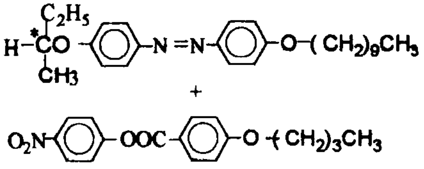
CHN analyzer and they have conformed with the theoretical values. FTIR: (Nujol, KBr pellets, cm^{-1}) Component A : 2925, 2853, 2599, 1496, 1241, 1146. 924, 845, 553.

Study

The components were weighed in known proportions and melted together in fusion tubes. They were thoroughly mixed in their melt to obtain a homogeneous mixture, after which they were cooled. This procedure was repeated three times. The solid obtained was finally ground and used for determining transition temperatures. The transition temperatures were determined by using a Leitz laborlux 12 POL polarizing microscope fitted with a Kofler heating stage.

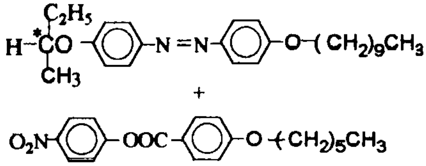
RESULTS AND DISCUSSION

Binary System -I: DPAB (A) + NPBB (B$_1$)



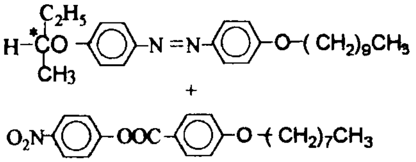
In this system (Table 1, Fig 1) both the components are non mesomorphic in nature. The mesogenic characteristic commences in monotropic nematic form with the addition of as low as 8 mole % A which becomes enantiotropic at 16mole% A. As the concentration of A increases to about 25mole% in the binary mixture the S_A phase emerges with the complete elimination of the nematic phase. This can be attributed to the fact that the terminal attractions are no longer sufficient to cause nematic orientations as layered orientations become predominent. The S_A phase is exhibited in the enantiotropic form till about 75mole% A after which it becomes monotropic at 87mole% A. The eutectic point is obtained at 48°C about 34 mole%A. Within the mixed mesophase region the S-I curve is in smooth continuation with the N-I curve & it deviates from linearity.

BINARY SYSTEM –II: DPAB (A) + NPHB (B_2)



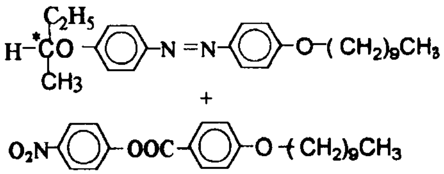
Phase diagram of this system (Table 2, Fig 2) shows that with the addition of about 8.5 mole%A of non-mesogen A to monotropic nematogen B_2, the mixture becomes enantiotropic nematic in nature and this trend continues up to about 17 mole% A, after which only smectic-A phase prevails. The S_A phase appears at 17 mole% A and the mixed smectic-nematic mesophase region is exhibited at this point only. Eutectic point is obtained at 50°C at about 36 mole% A showing a maximum mesophase range of around 35°C. The early appearance of smectic phase as compared to that in system I, can be attributed to the addition of two methylene units in the B_2 component, which provides added lateral adhesions. It is observed that two methylene units make a difference of about 8 mole% in terms of bringing the magnitude of lateral adhesions to the level of being effective for smectic mesophase to appear. In this system also N-I, S-I curves are in smooth continuation and they deviate from linearity, showing initially rising tendency upto 36 mole%A and then falling tendency upto about 88 mole%A.

BINARY SYSTEM III : DPAB (A) + NPOB (B_3)



This system (Table 3, Fig 3) consists of component A which is a chiral non-mesogen and B_3, which is polymesomorph, showing Sc and nematic phases. It is observed that on addition of as low as 9 mole%A the more ordered Sc changes to the less ordered S_A phase. As the concentration of component A increases in the mixture, it causes K-M transition to depress successively to a minimum of 42.5°C at about 38 mole % A which is the eutectic point of the system. The eutectic point is not a sharp point in this system but it is a rounded minimum on the curve as reported by us earlier[2]. The maximum mesophase range of 43.5°C is obtained at this molar concentration. In this system, the mixed S_A and nematic region exists up to 9 mole % A beyond which, on further addition of non mesogen A, the nematic phase is eliminated and smectic A phase predominates up to about 89 mole% A. In this system the continuous N-I and S-I curve rises up to about 38 mole% A, then it falls up to 89 mole% A, deviating from linearity.

BINARY SYSTEM IV: DPAB (A) + NPDB (B_4)



This system (Table 4, Fig 4) consists of components B_4, a smectogen, showing Sc phase and A, a non-mesogen. Addition of about 10 mole% of non-mesogen A to B_4 causes the more ordered smectic C phase to disappear with the commencement of the less ordered smectic A phase of focal conic fan shaped texture. The phase length of 43°C of S_A phase widens up to 39 mole%A after which it narrows down to 1.5°C at about 80 mole%A. In this system, as the molar concentration of component A increases in the mixture, it causes the K-M transition to depress successively to a minimum of 43^0C at about 30 mole%A and the S-I curve rises as the concentration of A increases in the mixture and then it shows a falling tendency upto about 90mole% A where S_A phase is exhibited in the monotropic form.

CONCLUSION

The study of these binary systems indicates that as the molecular geometry of the two components in the binary mixture differ, N-I, S-N & S-I curves deviate from their linear nature. The rising tendency could be due to different moieties of terminal groups and central bridges. Non linear behaviour of binary phase diagrams where one of the components has a strong polar end group have been reported by various workers earlier also.[9-11] In these binary systems, deviation from linearity rule can be attributed to nitro group's high tendency of favouring the formation of oriented fluids. Most of the textures show super cooling below 35°C.

ACKNOWLEDGEMENT

One of the authors, is thankful to the UGC for financial support.

Table 1: Binary system I

A + B_1

Mol%A	S_A	N	I
0	-	-	55
7.86	-	(54)	59
16.11	-	52	61
24.78	51	-	69
33.87	48	-	74
43.45	51	-	76
53.53	53	-	77
64.18	55	-	74
75.45	63	-	72
87.36	(64)	-	68
100		-	70

Table 2: Binary system II

A + B_2

Mol%A	S_A	N	I
0	-	(52)	68
8.5	-	55	64
17.29	52	65	71
26.39	52	-	82
35.81	50	-	85
45.55	52	-	83
55.65	60	-	81
66.12	62	-	76
76.99	67	-	69
88.29	(62)	-	70
100	-	-	70

( ) Values in parentheses indicate monotropic transitions

Table 3: Binary system III

A + B_3

Mol%A	S_A/Sc	N	I
0	49.0*	62	66
9.14	45.0	70	74.0
18.45	43.0	-	80.0
27.94	43.0	-	84.0
37.63	42.5	-	86.0
47.50	48.0	-	84.5
57.57	53.0	-	82.0
67.86	62.0	-	77.0
78.35	67.0	-	69.0
89.06	59.0	-	69.5
100.00	-	-	70.0

Table 4: Binary system IV

A + B_4

Mol%A	S_A/Sc	I
0	60.0*	78.0
9.76	52.0	81.5
19.56	43.5	83.8
29.44	43.0	86.0
39.34	44.0	87.0
49.32	51.0	86.0
59.34	60.0	82.0
69.42	65.0	76.0
79.56	68.0	69.5
89.75	62.0	70.0
100.00	-	70.0

* indicates Sc mesophase

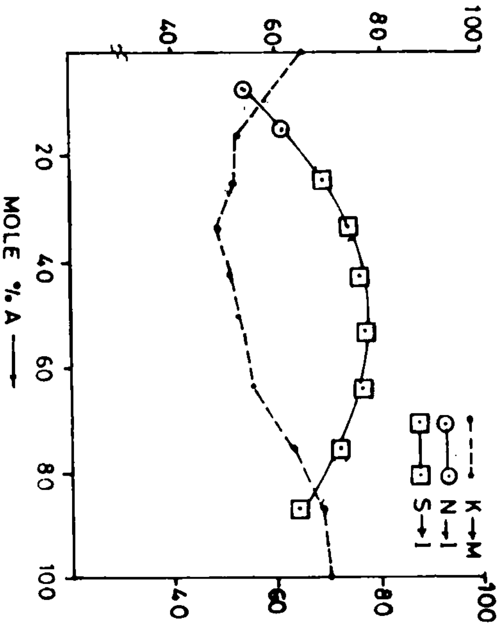


FIG.1 BINARY SYSTEM - I

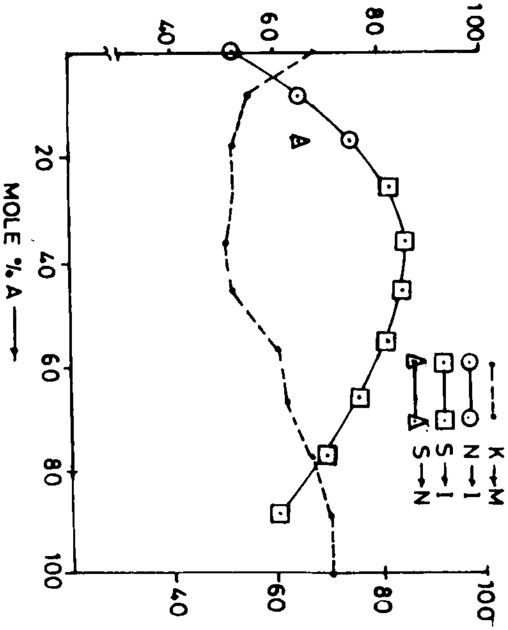


FIG. 2 BINARY SYSTEM - II

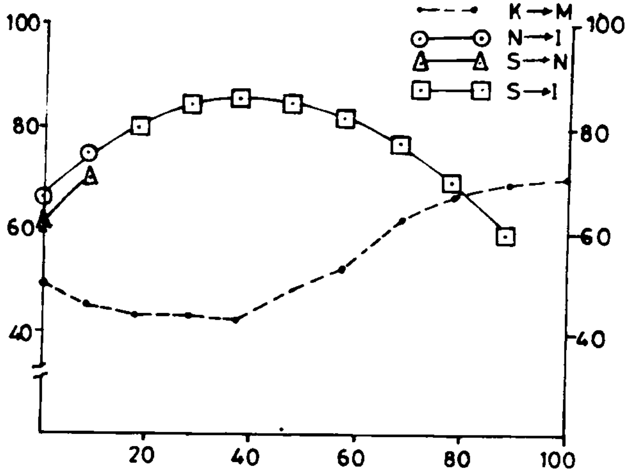


FIG. 3 BINARY SYSTEM - III

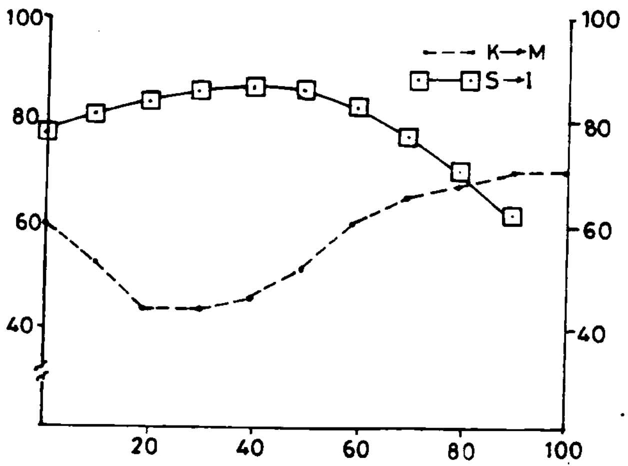


FIG. 4 BINARY SYSTEM - IV

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