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R. Mahajan [a] , H. Nandedkar [a] & V. Suthar [a]

[a] Applied Chemistry Department, Faculty of Technology and Engineering, M.S. University of Baroda, Post Box No. 51, Vadodara, 390 001

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Intermolecular Hydrogen Bonding in Mixed Mesomorphism

R. MAHAJAN, H. NANDEDKAR and V. SUTHAR

Applied Chemistry Department, Faculty of Technology and Engineering, M.S. University of Baroda, Post Box No. 51, Vadodara – 390 001

Exhibition of mixed mesophases in binary systems where both the components are non-mesogenic should offer a very interesting study because that should throw light on the mode of formation of mixed liquid crystal and factors favourably affecting it or otherwise. Five binary systems of non-mesogenic compounds were investigated for the induction of thermotropic mesophases. In three binary systems induced nematic and smectic mesophases are observed in number of compositions.

Keywords: Binary systems; induced mesophases; hydrogen bonding

INTRODUCTION

It has been pointed out that substances which do not individually form mesophases but which as binary mixture exhibit mixed mesomorphism, are generally very highly crystalline and are not readily supercooled from the liquid, therefore, monotropic mesophase which might have been anticipated may remain latent. If two such substances are mixed it may happen that the melting point of the mixture, which is generally lower than the melting point of the individual components falls below the mesophase-isotropic liquid temperature. Such a mixture may exhibit mesomorphism.

In recent years, the attention has been focused on the binary mixture in which induced mesophases are exhibited because of intramolecular hydrogen bonding[1-3]. The intermolecular hydrogen bonding must be an important contributing factor to maintaining the necessary aggregation for mesomorphism.

In the present study, the three binary systems where one of the components is Schiff's base possessing terminal nitro group, exhibit induced mesophases.

EXPERIMENTAL

[I] Synthesis of Schiff's bases.

1. 4 - nitro benzylidene - 4' - n - hexyloxy aniline (NBHA) was synthesized by method reported by Vora and Dixit.[4]
2. 4 - n - hexyloxy benzal - 4' - n - hydroxy aniline (HBHA) was synthesized as per the method reported by Goldmacher and MaCafferey.[5]

[II] Synthesis of Azo dyes.

The following three azo dyes were synthesized by the conventional method of diazotization and coupling.[6]

1. 4 - hydroxy - 4' - methyl azo benzene (HMeAB).
2. 4 - hydroxy - 4' - methoxy azo benzene (HMAB).
3. 4 - hydroxy - 4' - ethoxy azo benzene (HEAB).

[III] Preparation of Binary mixtures

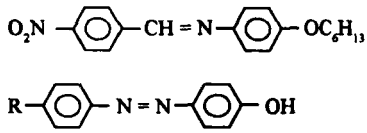
Binary mixtures were prepared by the standard method[7]. Transition temperatures were determined by using Leitz Labourlux 12 POL microscope provided with a heating stage.

RESULTS AND DISCUSSION

Two types of Binary Systems are studied.

A

Both the components belong to different homologous series. One of the components is Schiff's base possessing terminal Nitro group and the other component is an azo compound.



I : R = OCH_3 (HMAB).

II : R = OCH_2H_5 (HEAB).

III : R = CH_3 (HMeAB).

System I : NBHA : HMAB

Binary phase diagram (Fig I, System I) exhibits an induced monotropic nematic phase over a wide concentration range of mixed state.

System II : NBHA : HEAB

Fig. I, System II shows that as concentration of NBHA decreases an induced monotropic nematic phase appears at about 87 mole percent of NBHA and persists upto 15.6 mole percent of NBHA.

System III : NBHA : HMeAB

Table 2 indicates that no induced mesophases are observed when the alkoxy group i.e. ethoxy and methoxy groups of azo compound are replaced by Methyl group. No phases

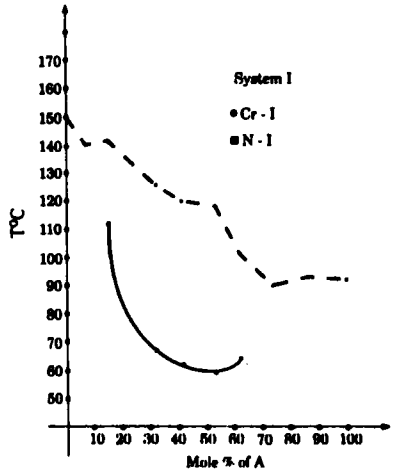
TABLE - 1. Transition Temperatures System I, II & IV

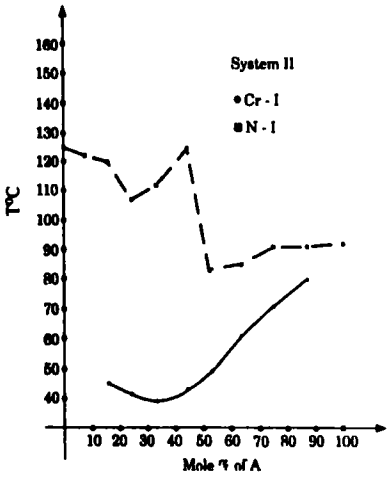
System	Mole % of A	Transition Temperatures °C S	N	I
I	100.00	—	—	92.0
	86.30	—	—	93.0
	73.66	—	—	90.0
	62.05	—	(64.0)	101.0
	53.17	—	(59.0)	118.0
	41.20	—	(62.0)	120.0
	31.84	—	(67.0)	126.0
	14.87	—	(112.0)	142.0
	7.20	—	—	140.0
	0.00	—	—	150.0

System	Mole % of A	Transition Temperatures °C S	N	I
II	100.00	—	—	92.0
	86.98	—	(80.0)	91.0
	74.80	—	(71.0)	91.0
	63.40	—	(61.0)	85.0
	52.69	—	(49.0)	83.0
	43.98	—	(43.0)	125.0
	33.09	—	(39.0)	112.0
	24.19	—	(41.0)	107.0
	15.64	—	(45.0)	120.0
	7.60	—	—	122.0
	0.00	—	—	125.0

System	Mole % of A	Transition Temperatures °C S	N	I
IV	100.00	—	—	92.0
	78.47	70.0	—	116.0
	68.00	70.0	—	121.0
	57.75	91.0	—	132.0
	47.66	75.0	—	124.0
	37.77	—	—	126.0
	28.08	—	—	137.0
	18.54	—	—	144.0
	9.17	—	—	160.0
	0.00	—	—	170.0

• Values in paranthesis indicate monotropy





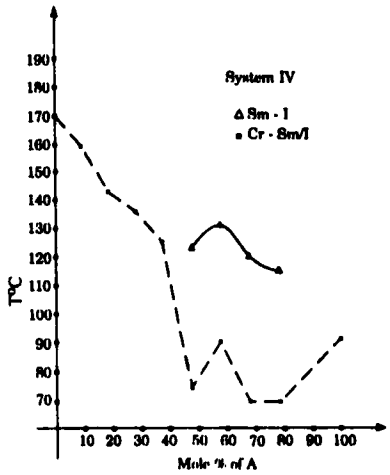


Figure 1

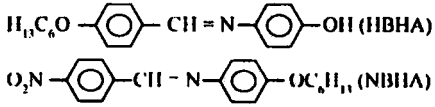
are observed even on quenching the mixtures. This behaviour may be attributed to less polarizability of methyl group as compared to methoxy and ethoxy terminal groups.

Table 2. Transition temperatures - System III

mole % of A	Melting point °C
100.00	92.0
70.06	116.0
58.38	114.0
50.42	128.0
37.53	130.0
28.51	140.0
20.48	146.0
13.05	151.0
6.24	153.0
0.00	159.0

B

Both the components belong to different homologous series. One of the components is Schiff's base possessing terminal hydroxy group.



System IV HBHA : NBHA

Both the components of Binary Systems are Schiff's bases. The phase diagram (Fig. 1. System IV) exhibits an induced enantiotropic smectic mesophase between 47.6 and 74.4 mole percent of NBHA. This further augments our earlier work[8] that even though the two components are "compatible" i.e. both have same central linkages, induced mesophases may be observed.

System V HBHA : HMAB

Few mixtures of this binary systems were prepared (Table 3.). No induced mesophases are observed. This may be attributed to the absence of strongly polar nitro group in the para position. Earlier studies[8,9] have also confirmed that the terminal nitro group plays a very important role in exhibition of induced mesophases.

Generally those non-mesogens possessing the structural characteristcs considered essential for exhibition of mesomorphism may be expected to show mixed mesomorphism. The large number of Schiff's bases fall in this catagory of non-mesogens; hence their binary mixtures have been studied. In the present study non-mesogenic azo compounds were used as one of the components.

The induced mesophases are observed in only some and not all of the binary systems studied may be because of factors such as polarity, polarizability, size of the molecule and their capacity of resisting their thermal breakdown on heating which also govern mesomorphism.

TABLE 3. Transition Temperatures - System V.

mole % of A	Melting point °C
100.00	170.0
66.15	135.0
56.57	120.0
46.48	112.0
35.83	108.0
0.00	150.0

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