Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl18

Exhibition of Induced Mesophases in the Binary Systems where One or Both the Components are Non-Mesogenic

R. A. Vora [a] , R. Gupta [a] & K. Patel [a]
[a] Applied Chemistry Department, Faculty of Technology and Engineering, M.S. University of Baroda, Post Box 51, Vadodara, 390 001, India
Version of record first published: 24 Sep 2006.

To cite this article: R. A. Vora , R. Gupta & K. Patel (1991): Exhibition of Induced Mesophases in the Binary Systems where One or Both the Components are Non-Mesogenic, Molecular Crystals and Liquid Crystals, 209:1, 251-263

To link to this article: http://dx.doi.org/10.1080/00268949108036200

Mol. Cryst. Liq. Cryst., 1991, Vol. 209, pp. 251–263
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

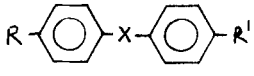
Exhibition of Induced Mesophases in the Binary Systems where One or Both the Components are Non-Mesogenic

R. A. VORA, R. GUPTA and K. PATEL

Applied Chemistry Department, Faculty of Technology and Engineering, M.S. University of Baroda, Post Box 51, Vadodara-390 001, India

(Received July 26, 1990)

A number of binary systems with induced smectic and/or nematic mesophases where one or both the components are mesogenic, have been reported by us.[1,2] To quantify the results, eight more binary systems of the types



where

R = $-OC_nH_{2n+1}$, $-NO_2$ R′ = $-NO_2$, $-COOC_nH_{2n+1}$, $-CH_3$
X = $-COO$, $-CH=N$

were studied. In the three binary systems of both non-mesogenic components, induced nematic and smectic mesophages are observed in number of compositions. In the binary system where one of the components is monotropic nematic, an induced smectic phase is observed and the monotropic nematic phase is converted to an enantiotropic phase. The remaining binary systems where one component exhibits a monotropic smectic mesophase, an enantiotropic smectic mesophase is observed at comparatively lower temperatures. The terminal nitro substituent is responsible for the induced mesomorphic behaviour in the binary systems of present investigation. The phase diagrams of the present study are discussed in detail and the common features emerging from the overall study are outlined to envisage such properties in the other systems.

Keywords: non-mesogens, induced mesophases, schiff bases

INTRODUCTION

In the present study we report number of binary systems where one or both the components are non-mesogenic. In all of the binary systems, one of the components is an ester and one of the components possesses polar nitro terminal group. Induced smectic and nematic mesophases are observed over a wide range of concentrations.

EXPERIMENTAL

1. Preparation of Compounds

(i) Iso-amyl p(p'-n-propoxybenzoyloxy) benzoate (APBB).

(ii) Iso-amyl p-(p'-n-butoxybenzoyloxy) benzoate (ABBB) were synthesized as described by Yadwadkar.[3]

(iii) p-(p'-n-propoxybenzoyloxy) nitrobenzene (PBNP).

(iv) p'-(p'-n-butoxybenzoyloxy) nitrobenzene (BBNB) were synthesized as described by Lohar and Dave for cinnamoyl derivatives.[4]

(v) p-(p'-n-pentyloxybenzoyloxy) toluene (PBT).

(vi) p-(p'-n-hexyloxybenzoyloxy) toluene (HBT) were synthesized as described by Dave and Vora.[5]

(vii) p-nitro benzylidene-p'-n-pentyloxyaniline (NBPA).

(viii) p-nitro benzylidene-p'-n-pentyloxyaniline (NBHA) were synthesized as described by Vora and Dixit.[6]

2. Preparation of Mixtures

The components were weighed in known proportion and melted together in fusion tubes. The mixtures were thoroughly mixed in the melt to obtain a homogeneous mixture. After cooling, the solid obtained was finely ground and was used for determining transition temperatures.

The transition temperatures were determined by using Leitz LaborLux 12 POL microscope.

The transition temperatures are given in Tables I to VIII. The plots of transition temperatures versus mole percent are given in Figures 1 to 8.

RESULTS AND DISCUSSION

Two types of binary systems are studied.

System I: Both of the components are non-mesogenic. Three systems were studied. Both of the components belong to different homologous series. One of the components possesses a nitro group while other component is an ester with $—CH_3$ or $—COOC_5H_{11}$ terminal group.

Ia: PBT + BBNB

Ib: APBB + BBNB

Ic: APBB + PBNB

System Ia: Binary phase diagram (Figure 1) exhibits an induced monotropic nematic phase between 68.8 to 89.5 mole percent concentration of BBNB.

System Ib: Figure 2 shows that as the concentration of BBNB decreases, an induced monotropic smectic phase appears even with as low as 10 mole percent

TABLE I

(*System Ia*)

A : $H_{11}C_5O$-⟨⟩-COO-⟨⟩-CH_3 (PBT)

B : H_9C_4O-⟨⟩-COO-⟨⟩-NO_2 (BBNB)

Mole % of B	Transition Temperatures °C	
	Nematic	Isotropic
0.00	—	70.0
9.50	—	79.0
19.10	—	79.0
28.80	—	81.0
38.70	—	80.0
48.65	—	76.0
58.70	—	74.0
68.80	(60.0)[a]	71.0
79.10	(58.0)	68.0
89.50	(53.0)	60.0
100.00	—	60.0

[a]Values in the parentheses indicate monotropy.

TABLE II

(*System Ib*)

A : H_7C_3O-⟨⟩-COO-⟨⟩-$COOC_5H_{11}$(iso) (APBB)

B : H_9C_4O-⟨⟩-COO-⟨⟩-NO_2 (BBNB)

Mole % of A	Transition Temperatures °C	
	Smectic	Isotropic
0.00	—	60.0
10.30	(48.9)[a]	59.5
17.39	51.7	54.9
24.30	(51.8)	53.5
37.13	60.6	69.4
46.14	60.1	68.9
54.74	(62.1)	65.6
65.77	(61.4)	67.6
78.57	(62.8)	66.2
85.67	—	64.8
100.00	—	77.0

[a]Values in the parentheses indicate monotropy.

TABLE III

(*System Ic*)

A: H_7C_3O-⟨⟩-COO-⟨⟩-$COOC_5H_{11}$ (iso) (APBB)

B: H_7C_3O-⟨⟩-COO-⟨⟩-NO_2 (PBNB)

Mole % of A	Transition Temperatures °C	
	Smectic	Isotropic
0.00	—	63.0
11.36	(41.0)[a]	58.1
18.08	(41.0)[a]	54.8
24.88	(42.0)[a]	60.0
35.95	(50.0)[b]	61.0
45.09	(52.8)	66.5
53.87	53.2	68.6
64.44	—	68.0
76.26	—	69.6
85.81	—	65.0
100.00	—	77.0

[a] Monotropic phases obtained on *quenching* only.
[b] Monotropic phases obtained on normal cooling.

TABLE IV

(*System IIa*)

A: $H_{13}C_6O$-⟨⟩-COO-⟨⟩-CH_3 (HBT)

B: H_9C_4O-⟨⟩-COO-⟨⟩-NO_2 (BBNB)

Mole % of B	Transition Temperatures °C		
	Smectic	Nematic	Isotropic
0.00	—	(53.0)[a]	64.0
9.90	—	(57.0)	67.0
19.85	—	(60.0)	66.0
29.80	(52.0)	61.0	66.0
39.80	(57.0)	63.0	68.0
49.80	(56.0)	62.0	69.0
59.80	(52.0)	59.0	68.0
69.80	(41.0)	55.0	68.0
79.80	—	53.0	69.0
89.90	—	53.0	59.0
100.00	—	—	60.0

[a] Values in the parentheses indicate monotropy.

TABLE V

(*System IIb*)

A: H_9C_4O-⟨⟩-COO-⟨⟩-$COOC_5H_{11}$ (iso) (ABBB)

B: H_9C_4O-⟨⟩-COO-⟨⟩-NO_2 (BBNB)

Mole % of A	Transition Temperatures °C	
	Smectic	Isotropic
0.00	—	60.0
7.09	(48.5)[a]	58.5
18.69	52.5	58.2
24.26	58.2	67.4
35.06	54.3	76.5
46.22	57.8	81.2
53.29	63.5	81.6
63.65	68.2	84.1
74.79	69.2	77.0
87.36	(64.4)	67.8
100.00	(68.0)	74.0

[a] Values in the parentheses indicate monotropy.

TABLE VI

(*System IIc*)

A: H_9C_4O-⟨⟩-COO-⟨⟩-$COOC_5H_{11}$ (iso) (ABBB)

B: H_7C_3O-⟨⟩-COO-⟨⟩-NO_2 (PBNB)

Mole % of A	Transition Temperatures °C	
	Smectic	Nematic
0.00	—	63.0
8.56	(40.0)[a]	63.0
16.97	(43.0)[a]	55.0
25.17	(51.7)[b]	59.0
34.47	53.0	55.0
45.43	61.0	66.7
55.84	63.0	71.1
65.09	64.5	77.0
75.88	(62.0)	65.0
88.90	(59.0)	62.0
100.00	(68.0)	74.0

[a] Monotropic values obtained on *quenching* only.
[b] Monotropic values obtained on normal cooling.

TABLE VII

(*System IId*)

A : H_9C_4O-⟨○⟩-COO-⟨○⟩-$COOC_5H_{11}$ (iso) (ABBB)

B : O_2N-⟨○⟩-CH:N-⟨○⟩-OC_6H_{13} (NBHA)

Mole % of A	Transition Temperatures °C	
	Smectic	Isotropic
0.00	—	94.0
8.60	—	97.0
17.50	(88.0)[a]	95.0
26.70	89.0	98.0
36.10	96.0	104.0
45.90	97.0	104.0
56.02	96.0	103.0
66.50	87.0	103.0
77.30	76.0	92.0
88.40	71.0	82.0
100.00	(68.0)	74.0

[a] Values in the parentheses indicate monotropy.

TABLE VIII

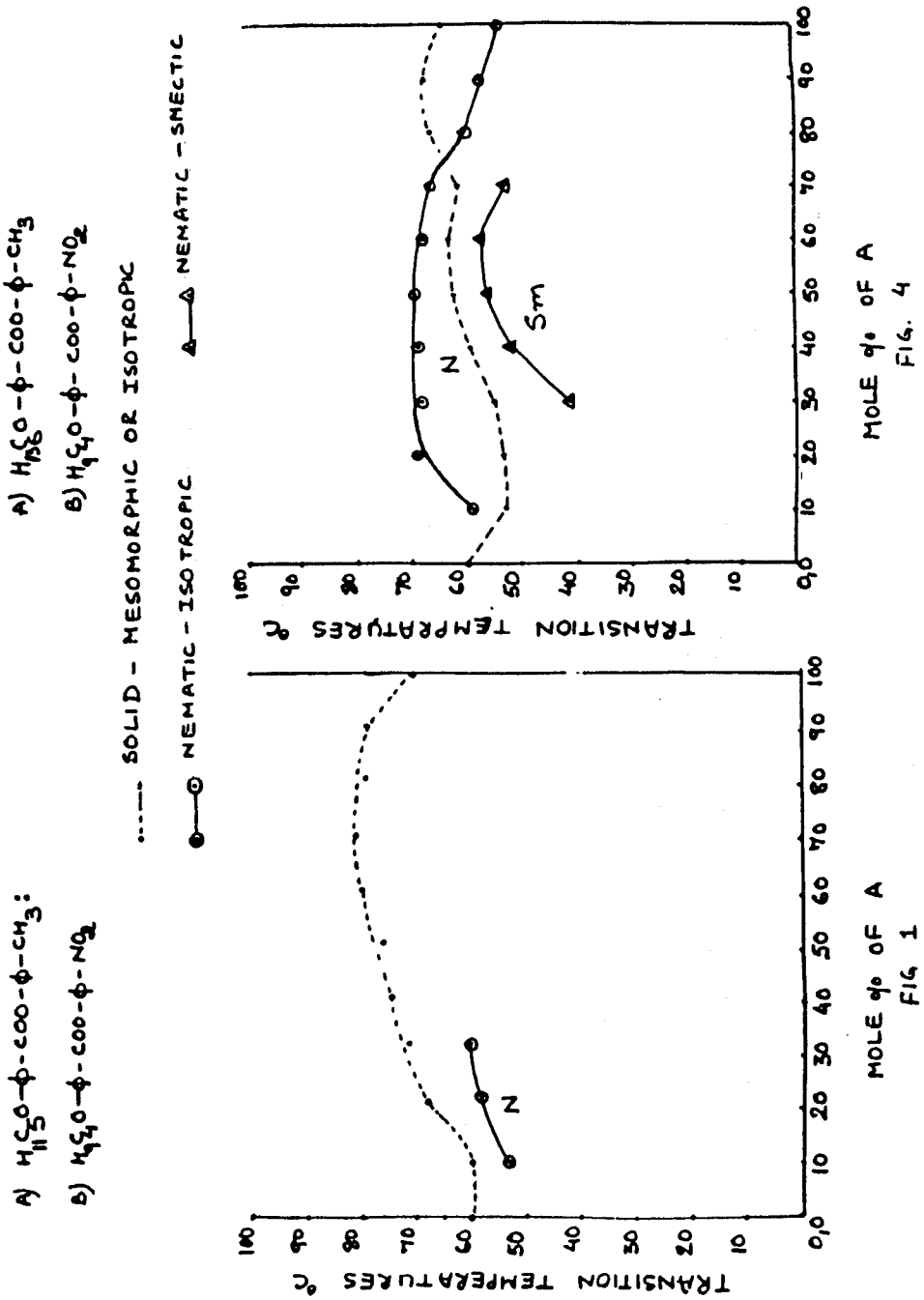
(*System IIe*)

A : H_9C_4O-⟨○⟩-COO-⟨○⟩-$COOC_5H_{11}$ (iso) (ABBB)

B : O_2N-⟨○⟩-CH:N-⟨○⟩-OC_5H_{11} (NBPA)

Mole % of A	Transition Temperatures °C	
	Smectic	Isotropic
0.00	—	89.0
8.30	(82.0)[a]	90.0
16.90	(84.0)	91.0
25.80	85.0	103.0
35.14	96.0	108.0
44.80	96.0	104.0
59.90	94.0	103.0
65.50	88.0	102.0
76.5	72.0	95.0
87.9	71.0	84.0
100.00	(68.0)	74.0

[a] Values in the parentheses indicate monotropy.



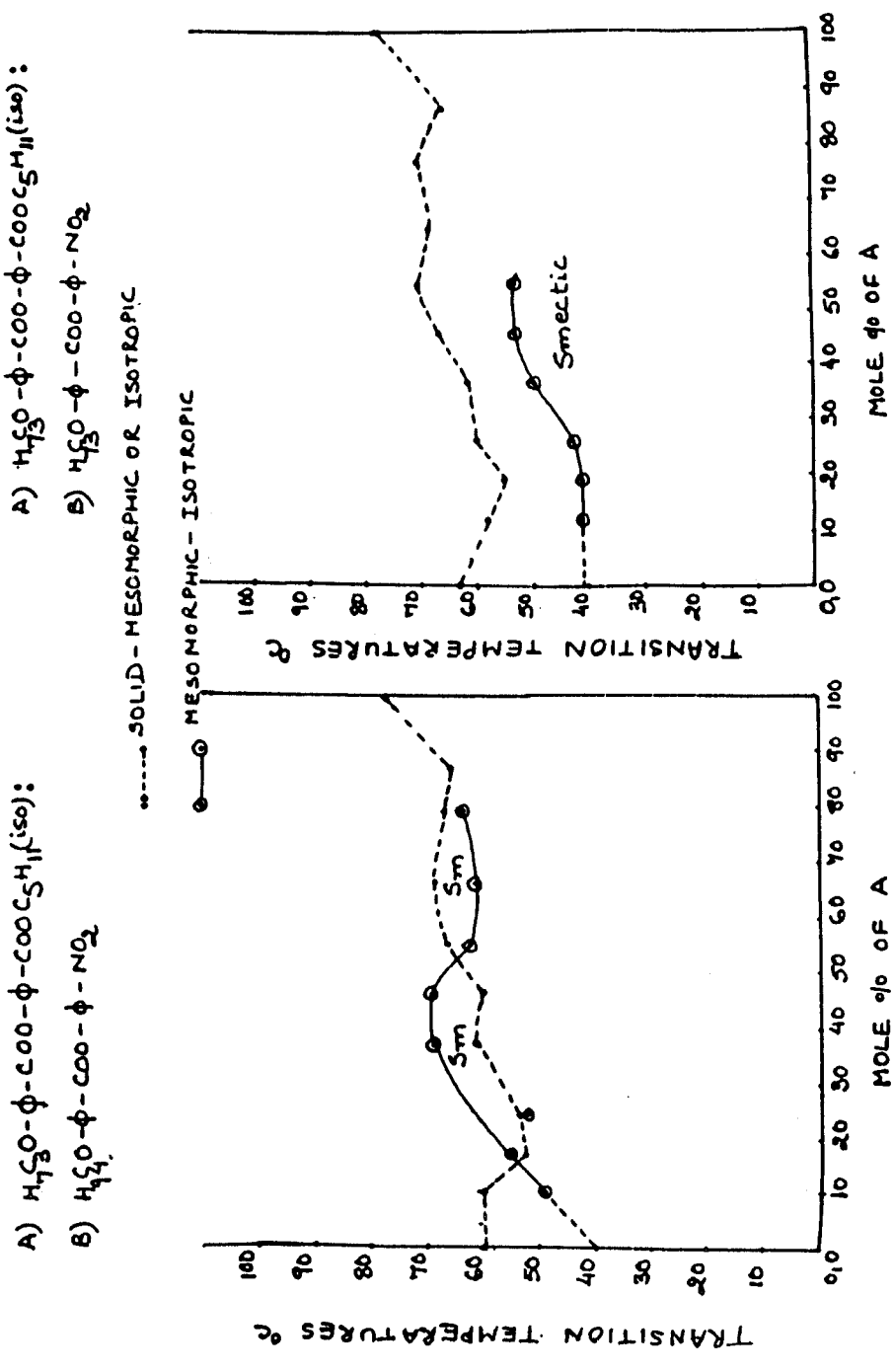


FIG. 2

FIG. 3

A) $HC_{9}C_{4}O-\phi-COO-\phi-COOC_5H_{11}$(iso):

B) $HC_{9}C_{4}O-\phi-COO-\phi-NO_2$

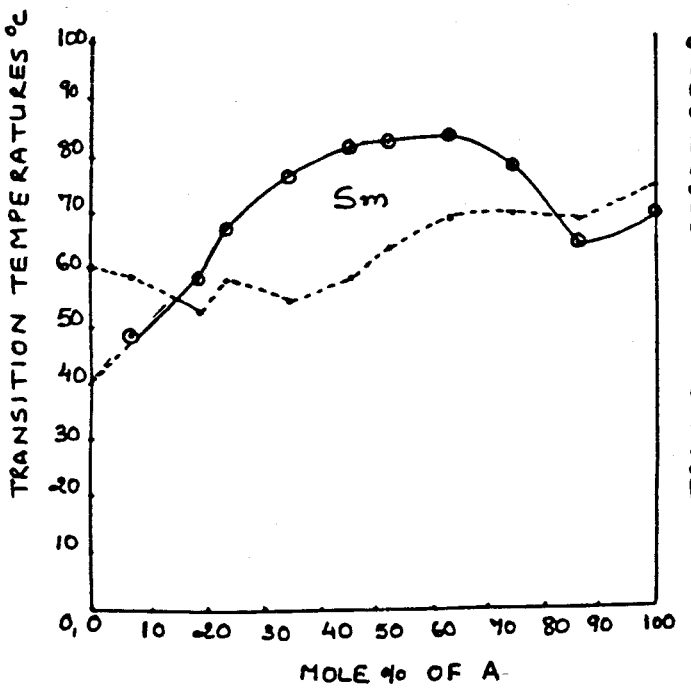


FIG. 5

A) $HC_{9}C_{4}O-\phi-COO-\phi-COOC_5H_{11}$(iso):

B) $HC_{13}O-\phi-COO-\phi-NO_2$

SOLID - MESOMORPHIC OR ISOTROPIC

MESOMORPHIC - ISOTROPIC

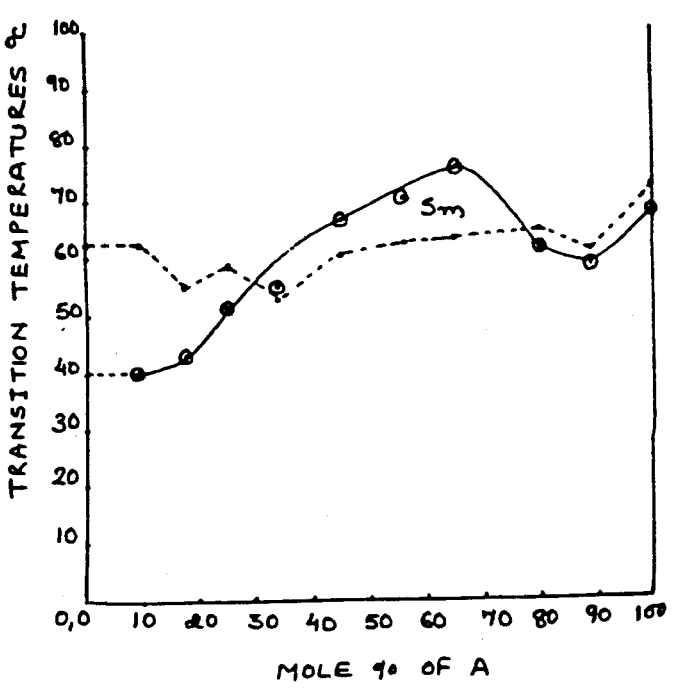


FIG. 6

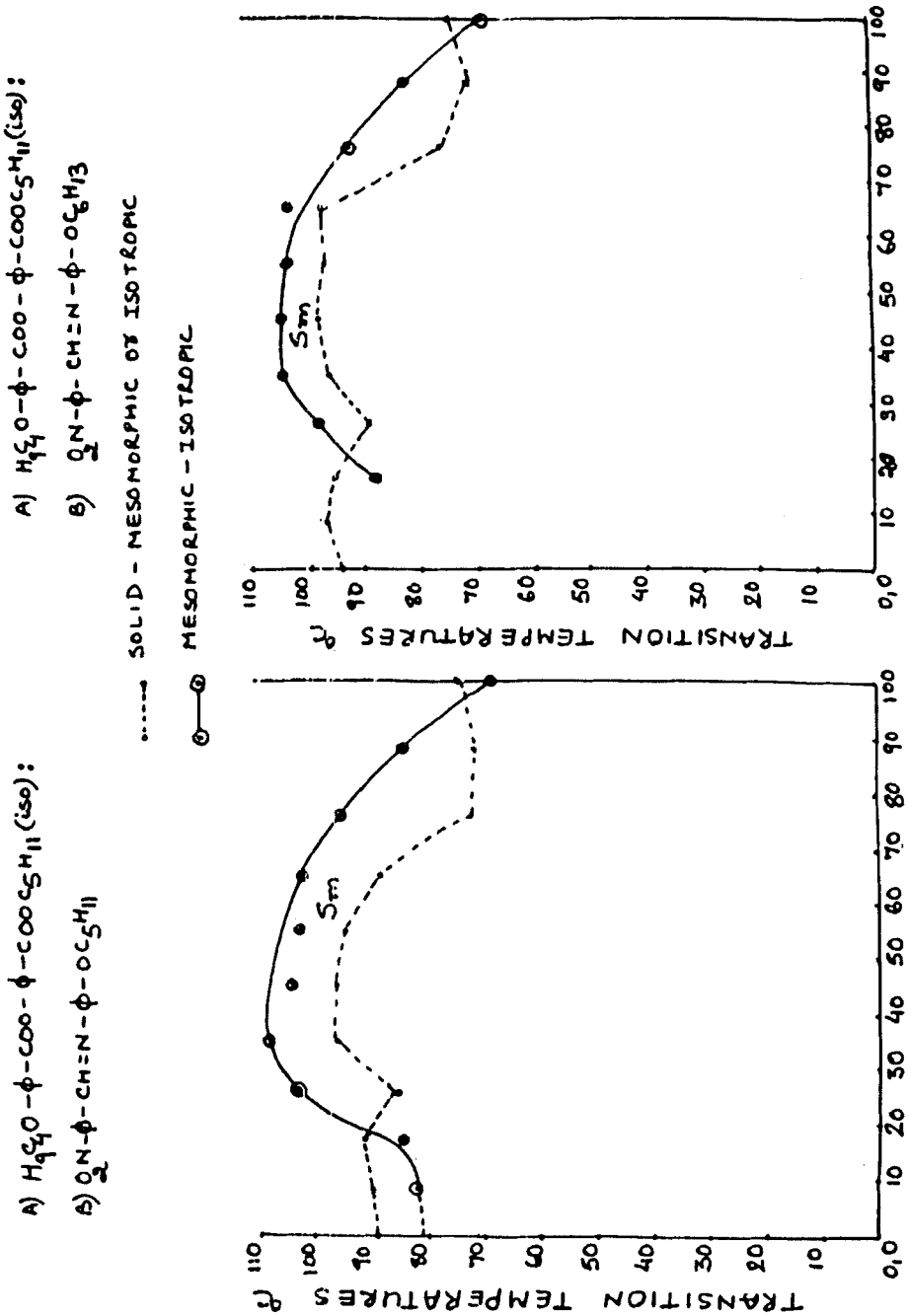


FIG. 8

FIG. 7

concentration of APBB. With further decrease in the concentration of BBNB, the monotropic mesophase becomes enantiotropic. At about 45 mole percent of BBNB, the transition becomes monotropic and at about 14 mole percent concentration of BBNB the system becomes non-mesogenic. The smectic-isotropic transition temperature curve is extrapolated on the side where monotropic smectic phase is observed to find the latent transition temperature of BBNB. The latent transition temperature for BBNB, obtained by this method is 40°C. It has been reported that the extrapolation method of finding the latent transition temperature is more reliable if monotropic mesophases are observed up to a certain concentration range.[7-10]

System Ic: The two non-mesogens exhibit an induced smectic mesophase in the mixed state over a wide concentration range. With as low as 11 mole percent concentration of APBB, an induced smectic phase is observed at 41°C on quenching. On slow cooling crystallization takes place before the commencement of mesophase. While a normal monotropic smectic phase is observed between 36 to 54 mole percent concentration of APBB, further increase in APBB concentration renders the system non-mesogenic. The latent transition temperature for PBNB obtained by extrapolation method is 41°C (Figure 3).

System II: One of the components is monotropic nematic or smectic and the other is non-mesogenic.

Five binary systems were studied, where one of the components is either a Schiff base or an ester possessing nitro group while the other component is an ester.

IIa: HBT + BBNB

IIb: ABBB + BBNB

IIc: ABBB + PBNB

IId: ABBB + NBHA

IIe: ABBB + NBPA

System IIa: The binary phase diagram (Figure 4) exhibits two eutectic points and between these eutectic points, the system exhibits an enantiotropic nematic and a monotropic smectic mesophases. The nematic-isotropic as well as the isotropic-smectic transition temperature curve exhibit maxima.

The difference between the systems Ia and IIa is that the component A in the system Ia is a lower homologue, but there is a surprising difference in the behaviour of two systems. System Ia does not exhibit the rich mesomorphism exhibited by system IIa.

Systems IIb and IIc: The binary phase diagram of System IIb (Figure 5) exhibits a smectic mesophase over a very wide range of mixed composition. Even with as low as 8 mole percent concentration of ABBB, a monotropic smectic phase is observed, which becomes enantiotropic phase between the two eutectic points and beyond that the system exhibits monotropic smectic phase.

The system IIc (Figure 6) exhibits a smectic mesophase from about 8 mole percent concentration of ABBB. Between 8 to 17 mole percent concentration of ABBB, a smectic mesophase is obtained at 40°C on cooling suddenly, and on slow cooling crystallization takes place. Between 40–70 mole percent concentration of ABBB, the system becomes enantiotropic and at higher concentration of ABBB, the system again becomes monotropic smectic.

Systems IId and IIe: The binary phase diagram for system IId (Figure 7) exhibits two eutectic points and a smectic mesophase over most of the composition range. An interesting feature of this system is that between the two eutectics, the melting point as well as the crystal-smectic transition temperature rise. The extrapolation of smectic-isotropic transition temperature curve gives the latent transition temperature for the non-mesogenic component (NBHA) as 81°C, which agrees well with the values obtained by Gupta and Vora.[1]

Binary system IIe (Figure 8) also exhibits two eutectic points and maxima for solid-smectic and smectic-isotropic transition temperatures. The compositions between two eutectics exhibit enantiotropic smectic phases. A monotropic smectic mesophase is observed even with 8 mole percent concentration of component ABBB.

CONCLUSION

The binary systems studied, where one of the components possesses nitro terminal group, exhibit an induced smectic mesophase. In the earlier work,[1] two 'incompatible' components, i.e., one with an ester linkage and the other with an azomethine linkage were examined and induced mesophases were obtained. In the present work, even though the two components are 'compatible,' i.e., both have central ester linkage, induced mesophases are exhibited by the binary systems and the enhancement in the smectic phase is highly pronounced.

Acknowledgment

The authors are thankful to the Dean, Faculty of Technology and Engineering for his interest in the work. RG and KP are also thankful to Head, Applied Chemistry Department for providing the research facilities. One of the authors (Renu Gupta) sincerely acknowledges the INSA Bursary grant provided by Indian National Science Academy.

References

1. Renu Gupta and R. A. Vora, *Mol. Cryst. Liq. Cryst.*, **106**(1–2), 147 (1984).
2. Renu Gupta, Presented at the 11th International Liquid Crystal Conference, University of California, Berkeley, U.S.A. (1986).
3. Shashikala Yadwadkar, Ph.D. Thesis, M.S. University of Baroda, Baroda (1983), pp. 57, 80.
4. J. M. Lohar and Jayrang Dave, *Mol. Cryst. Liq. Cryst.*, **103**(1–4), 143 (1983).
5. Dave, J. S. and Vora, R. A., Pramana, Suppl. No. 1, 1975, p. 447.

6. Vora, R. A. and Dixit, N., "Liquid Crystals," Ed. S. Chandrasekhar, Heyden, London, (1980), p. 585.
7. Dave, J. S., Patel, P. R. and Vasanth, K. L., *Ind. J. Chem.*, **4**, 505 (1966); *Mol. Cryst. Liq. Cryst.*, **8**, 93 (1966).
8. Dave, J.S. and Vasanth, K. L., *Ind. J. Chem.*, **7**, 498 (1986).
9. Dave, J. S. and Dewar, M. J. S., *J. Chem. Soc.* 4617 (1954); 4305 (1955).
10. Lohar, J. M. and Shah, D. S., *Mol. Cryst. Liq. Cryst.*, **28**, 293 (1974).