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Binary Mesogenic Systems Comprised of Ester Mesogens and Non-Mesogens

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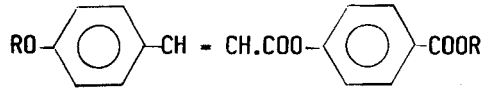
With a view to evaluate the effect of non-mesogen or mesogen on the binary systems comprised of a nematogon or a polymesomorph, the present study was undertaken where the compounds have general structure (I):



I

R = —CH_3, —C_2H_5, —C_3H_7, and —C_4H_9.
R′ = —C_4H_9, —C_5H_{11}.

The binary systems are selected with variation in R and R′ (I). The binary phase diagrams have very interesting behaviour. One most common feature is rounded minimum of melting point curve suggesting large depression and resulting into ambient temperature mesophase. A non-mesogen as one of the components decreased the mesomorphic tendency of the system and, in some cases, rendered the enantiotropic phase to monotropic phase with one exception. The binary systems comprised of mesogen and polymesogen exhibited interesting behaviour. The nematic phase remained enantiotropic for most of the compositions but the nematic-smectic curve went on falling up to about 50% concentration and then the phase was eliminated from the system. Whereas in the second binary system, the monotropic-smectic phase is converted to enantiotropic phase. The common feature with one exception is that the difference in the value of R(I) in binary system depresses the solid-mesomorphic transition temperatures markedly. The smectogenic tendencies are enhanced with increasing carbon chain of alkoxy and ester substituent keeping with the trend observed in homologous series.

Keywords: ester mesogens, induced smectic phase, polymesogenic

INTRODUCTION

A number of binary systems have been reported in the literature.[1–3] Some of these binary systems have brought out new phenomena[4,5] and also induced mesomorphism.[6,7] The binary and ternary mixtures of mesogens have provided better formulations for applications in different fields. This has given impetus for the studies of binary and ternary systems comprised of mesogens and non-mesogens.

TABLE I

System No. I
Component A: n-Butyl p-(p'-methoxycinnamoyloxy) benzoate
B: n-Butyl p-(p'-ethoxycinnamoyloxy) benzoate

Mole percent of component A	Transition		Temperatures (°C)
	S	N	I
00.00	76.0	85.0	92.5
10.35	71.0	75.0	89.0
20.62	68.0	72.0	85.0
32.84	(65.5)	66.0	83.0
40.93	(64.5)	65.0	78.0
50.96	—	67.0	76.5
60.92	—	68.0	69.0
70.80	—	(69.0)	70.0
80.61	—	(70.0)	73.0
90.35	—	(66.0)	75.0
100.00	—	—	79.0

Values in parentheses indicate monotropy.

TABLE II

System No. II
Component A: n-Butyl p-(p'-methoxycinnamoyloxy) benzoate
B: n-Amyl p-(p'-methoxycinnamoyloxy) benzoate

Mole percent of component A	Transition		Temperatures (°C)
	S	N	I
00.00	—	(76.0)	88.0
11.32	—	(77.5)	86.5
20.63	—	(77.0)	85.0
30.93	—	(76.0)	81.5
39.93	—	(75.0)	79.0
50.97	—	(74.5)	76.0
59.94	—	(73.5)	74.0
70.81	—	67.0	70.0
80.62	—	(71.5)	72.0
90.35	—	(72.0)	76.0
100.00	—	—	79.0

Values in parentheses indicate monotropy.

EXPERIMENTAL

Compounds having the following general formula were synthesized by the known method.[10]

Where

$$R = CH_3, C_2H_5, n\text{-}C_3H_7, n\text{-}C_4H_9$$

$$R' = n\text{-}C_4H_9, n\text{-}C_5H_{11}$$

Binary mixtures were prepared by the standard method.[11] Transition temperatures were determined by using a polarizing microscope provided with FP-2 hot stage. The transition temperatures of these systems are given in Tables I–VI.

TABLE III

System No. III
Component A: n-Butyl p-(p'-methoxycinnamoyloxy) benzoate
B: n-Amyl p-(p'-ethoxycinnamoyloxy) benzoate

Mole percent of component A	Transition		Temperatures (°C)
	S	N	I
00.00	(86.0)	87.0	97.5
11.89	(72.0)	80.0	92.0
20.81	(68.0)	76.0	87.0
31.63	—	68.0	83.0
42.88	—	61.0	78.5
51.91	—	59.0	77.5
61.82	—	57.0	76.5
71.58	—	60.5	75.0
81.20	—	68.0	74.0
10.67	—	—	76.0
100.00	—	—	79.0

Values in parentheses indicate monotropy.

TABLE IV

System No. IV
Component A: n-Amyl p-(p'-ethoxycinnamoyloxy) benzoate
B: n-Amyl p-(p'-methoxycinnamoyloxy) benzoate

Mole percent of component A	Transition		Temperatures (°C)
	S	N	I
00.00	—	(76.0)	88.0
9.67	—	(81.0)	86.0
19.41	—	(82.5)	83.5
31.20	—	75.0	82.5
39.11	—	70.5	81.5
51.07	—	62.0	83.5
59.11	(55.0)	59.5	85.0
70.22	(65.0)	74.0	89.0
80.40	(76.0)	81.5	91.5
90.34	(82.0)	85.0	94.5
100.00	(86.0)	87.0	97.5

Values in parentheses indicate monotropy.

TABLE V

System No. V
Component A: n-Amyl p-(p'-ethoxycinnamoyloxy) benzoate
B: n-Amyl p-(p'-propoxycinnamoyloxy) benzoate

Mole percent of component A	Transition		Temperatures (°C) I
	S	N	
00.00	78.0	82.0	87.0
9.64	76.0	80.0	86.5
19.43	75.5	79.5	86.0
31.22	75.0	79.0	85.5
41.12	76.0	81.0	87.5
49.10	77.0	82.0	80.0
58.13	78.0	82.0	90.5
69.23	79.5	83.5	90.5
77.37	82.0	84.5	92.5
87.61	85.0	86.0	94.5
100.00	(86.0)	87.0	97.5

Values in parentheses indicate monotropy.

TABLE VI

System No. VI
Component A: n-Amyl p-(p'-ethoxycinnamoyloxy) benzoate
B: n-Amyl p-(p'-butoxycinnamoyloxy) benzoate

Mole percent of component A	Transition		Temperatures (°C) I
	S	N	
00.00	72.0	—	105.0
12.72	70.0	—	104.5
21.14	67.0	95.0	104.0
31.50	60.0	92.0	103.5
41.71	59.0	90.5	103.5
51.76	65.5	87.5	103.0
61.69	68.5	86.0	102.5
71.47	73.5	84.0	102.5
79.17	78.5	83.0	101.0
90.65	(84.0)	85.0	98.5
100.00	(86.0)	87.0	97.5

Values in parentheses indicate monotropy.

RESULTS AND DISCUSSIONS

Binary System I: Non-Mesogen + Polymesogen

Component A: n-Butyl p-(p'-methoxycinnamoyloxy) benzoate (BMCB)

$$K \xrightarrow{79} I$$

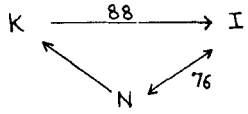
Component B: n-Butyl p-(p'-ethoxycinnamoyloxy) benzoate.

$$K \xrightarrow{76} Sm \xrightarrow{85} N \xrightarrow{92} I$$

The phase diagram is obtained by plotting mole percent composition of component A versus transition temperatures (Figure 1). Enantiotropic-smectic phase of component B becomes monotropic and is eliminated from the system when mole percent composition of component A reaches to 40 percent. The nematic-isotropic transition temperature curve falls steeply and nematic phase becomes monotropic before it is eliminated from the system at about 85 percent concentration of component A. The solid-mesogenic transition temperature curve exhibits rounded minimum.

Binary System II: Non-mesogenic + Nematic

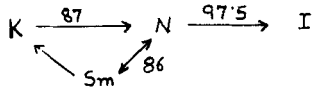
Component A: B M C B
Component B: n-Amyl p-(p'-methoxycinnamoyloxy) benzoate.



The binary phase diagram (Figure 2) shows that the monotropic-nematic phase becomes enantiotropic at the eutectic point then again becomes monotropic. The mesogenic behaviour is observed up to about 85 mole percent concentration of component A.

Binary System III: Non-mesogenic + Polymesogenic

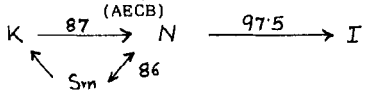
Component A: B M C B
Component B: n-Amyl p-(p'-ethoxycinnamoyloxy) benzoate.



The binary phase diagram (Figure 3) shows that nematic phase of component B persists up to about 85 mole percent composition of component A. The smectic phase survives only 25 mole percent composition of component A. The solid-mesogenic transition temperature curve exhibits rounded minimum and the maximum drop in the S-M transition is about 25°C.

Binary System IV: Polymesogenic + Nematic

Component A: n-Amyl p-(p'-ethoxycinnamoyloxy) benzoate.



SYSTEM- 1

p-n BUTYL (p'- METHOXY CINNAMOYLOXY) BENZOATE: p-n-BUTYL (p'- ETHOXY CINNAMOYLOXY)-BENZOATE

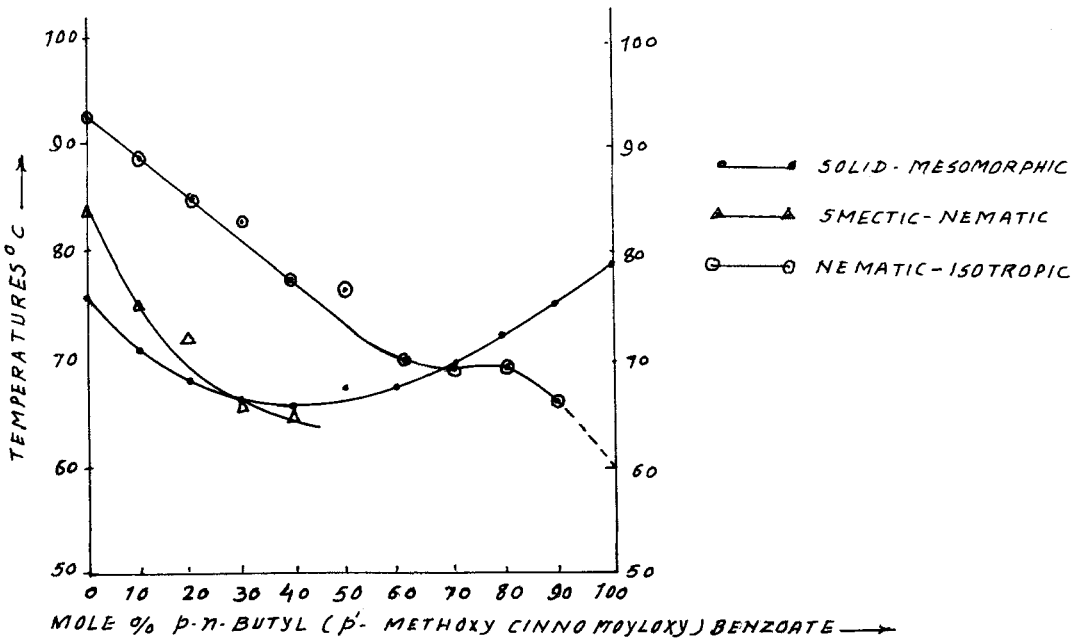


FIGURE 1

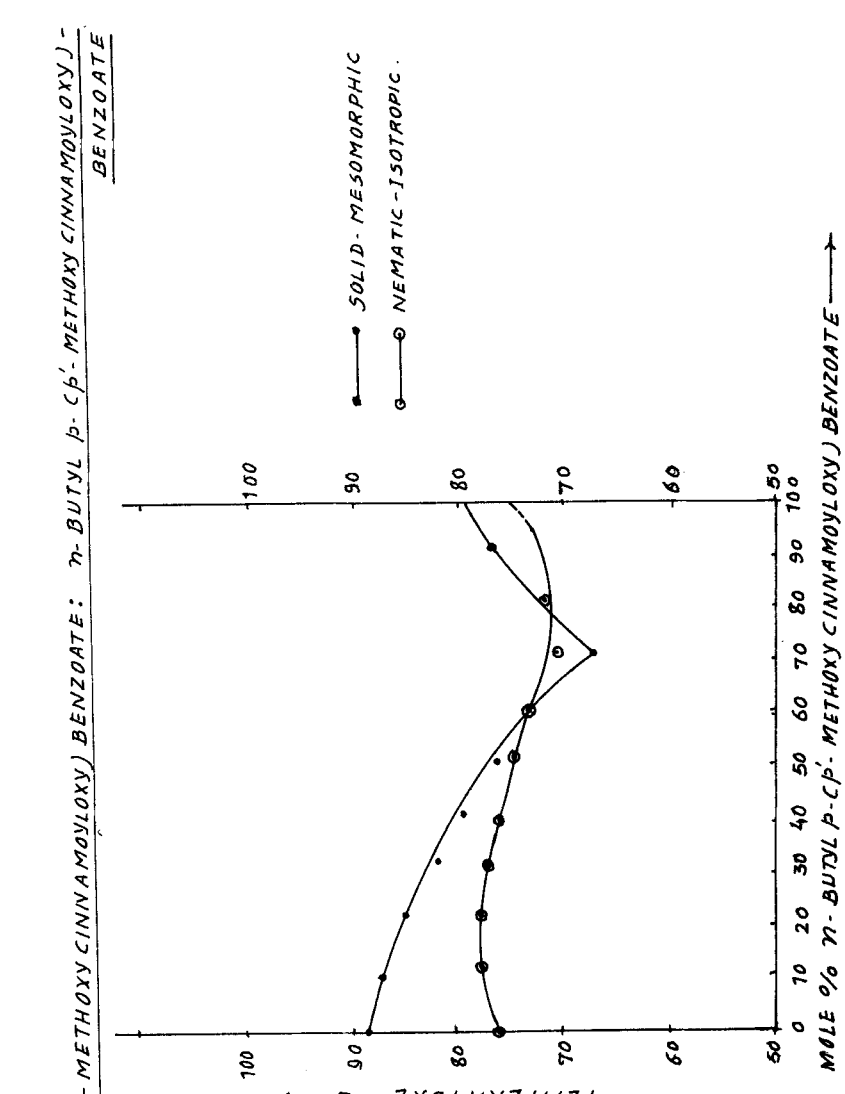


FIGURE 2

SYSTEM-3

n-AMYL p (p'-ETHOXY CINNAMOYLOXY) BENZOATE : n-BUTYL p-(p'-METHOXY CINNAMOYLOXY)-BENZOATE

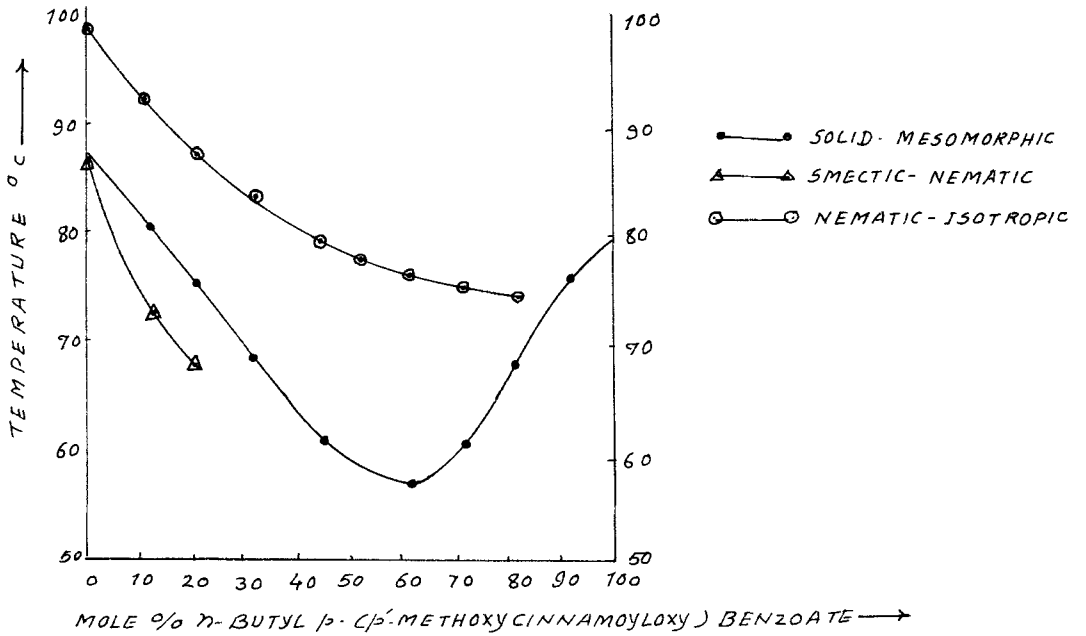
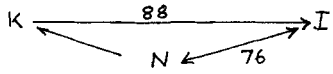


FIGURE 3

Component B: n-Amyl p-(p′-methoxycinnamoyloxy) benzoate.



The binary phase diagram (Figure 4) shows that as the concentration of component B increases the monotropic-nematic phase is changed to an enantiotropic one. The behaviour of the isotropic-smectic curve is very typical. It falls steeply up to the 40 mole percent concentration of component B and the phase gets eliminated from the system. The drop in the isotropic-nematic phase is about 31°C. Normally when the solid-mesogenic transition temperature curve exhibits eutectic with good depression, one would expect monotropic becoming enantiotropic in nature at least for the small range of concentration. Instead of this normal behaviour in system IV, the isotropic-smectic transition temperatures continue falling and subsequently are eliminated.

Binary System V: Polymesogenic + Polymesogenic

Component A: A E C B

Component B: n-Amyl p-(p′-n-propoxycinnamoyloxy) benzoate.

$$K \xrightarrow{78} Sm \xrightarrow{82} N \xrightarrow{87} I$$

As the binary phase diagram indicates, the behaviour is quite normal. The smectic phase becomes enantiotropic with even a small amount of component B. The solid-mesomorphic transition temperature curve neither shows any eutectic behaviour nor much depressed rounded minimum (Figure 5).

Binary System VI: Polymesogenic + Smectic

Component A: A E C B

Component B: n-Amyl p-(p′-n′-butoxycinnamoyloxy) benzoate.

$$K \xrightarrow{72} Sm \xrightarrow{105} I$$

The component B, a smectogen, is mixed with a polymesogen component A having monotropic phase. As expected, binary phase diagram (Figure 6) exhibits enantiotropic phases as the concentration of component B increase in the binary mixture. The nematic phase makes its appearance even with 20 mole percent concentration of component A. The results indicate that binary phase diagram exhibits polymesogenic behaviour for the large range of composition of the system. The eutectic point is depressed and is at about 50°C.

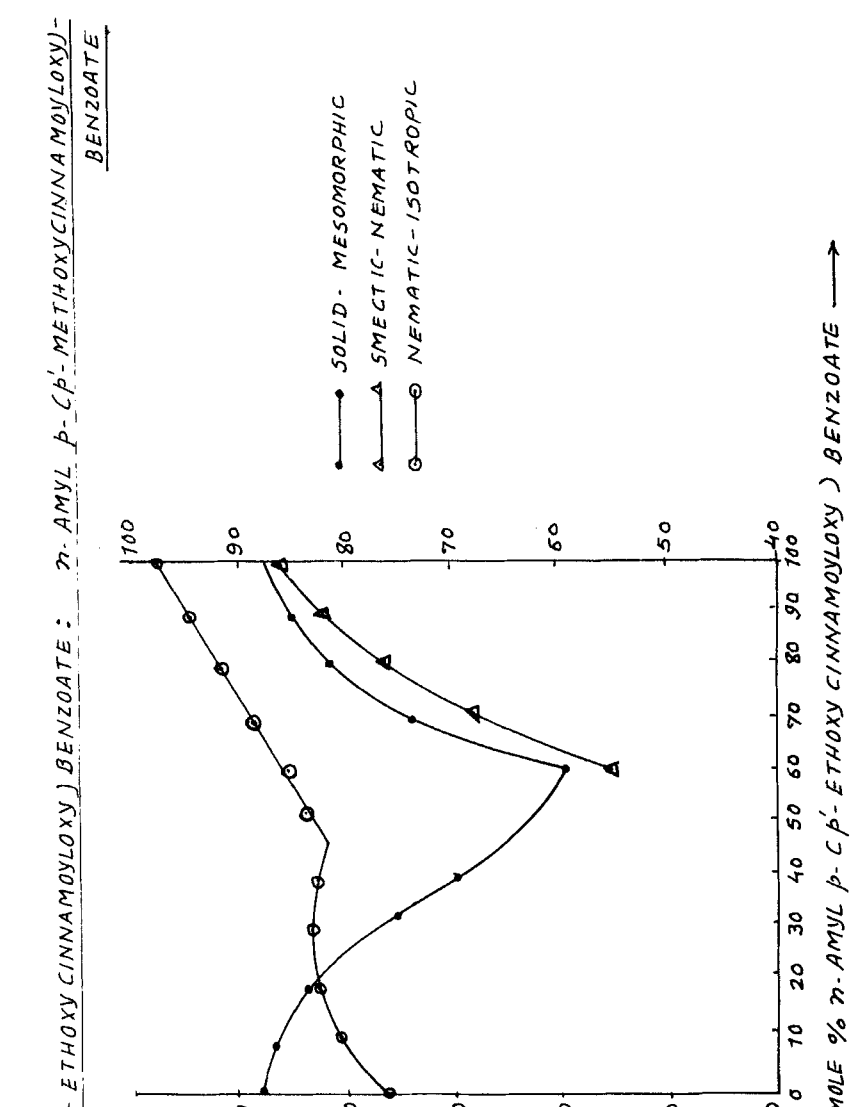


FIGURE 4

SYSTEM- 5

p-n-AMYL (p'-ETHOXY CINNAMOYLOXY) BENZOATE : p-n-AMYL (p'-PROPOXY CINNAMOYLOXY)-BENZOATE

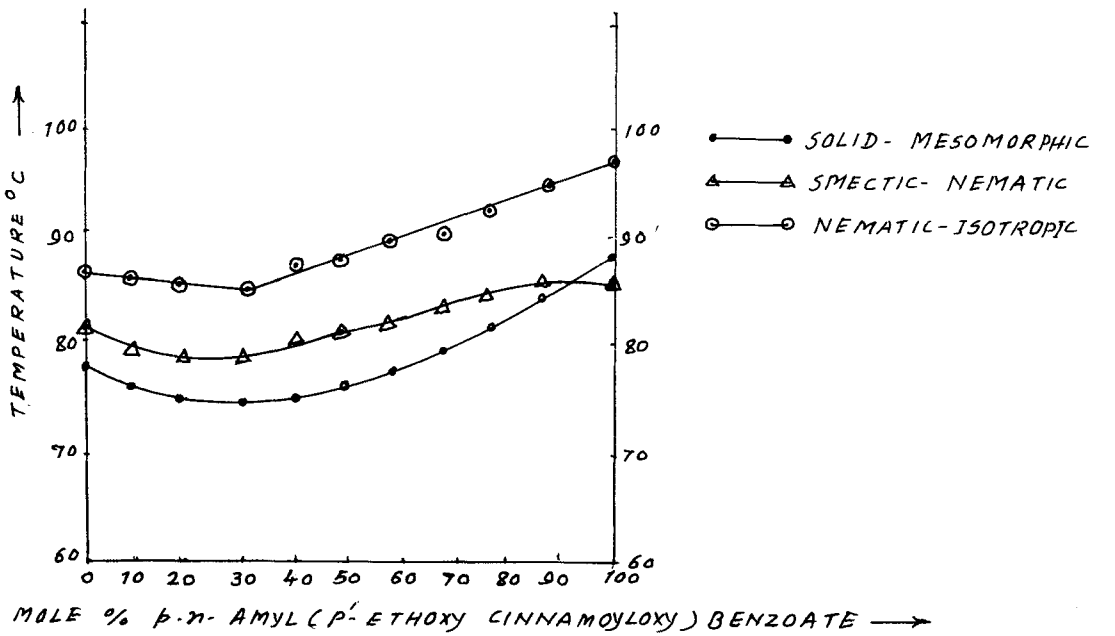


FIGURE 5

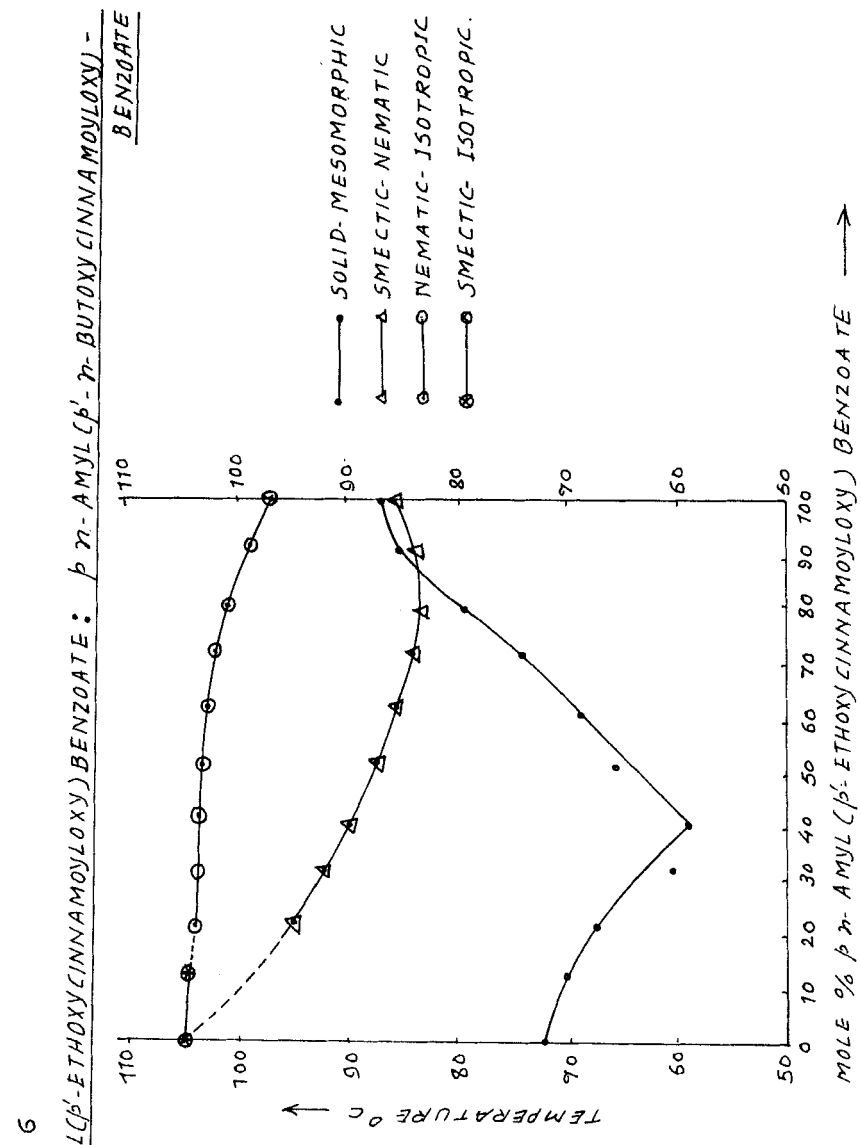


FIGURE 6

Common Features of Binary Systems I to VI.

Systems I to III have the common component BMCB. In these systems, the nematic mesophase is stabilized but the smectic phase is destabilized.

This is also observed when the chain length is increased from butyl to amyl. This indicates that the ethoxy group predominantly plays its role in favouring the nematic phase. The group-efficiency order obtained by Dave and Vora[12] indicates that the ethoxy group has a strong tendency in promoting the nematic phase in the mixed mesomorphism. Hence, the present findings indicate that even in polymesogenic compounds, behaviour of the ethoxy group is maintained. In the case of system II, the methoxy group of both components enhance nematogenic tendency making it enantiotropic for a small concentration range. This is also expected as the methoxy group has a strong tendency to promote nematogenic tendencies.[12]

In the case of systems IV to VI, the component AECB is common, exhibiting monotropic smectic and enantiotropic nematic phases, the second component is either a nematogen (System IV), polymesogen (System V) or a smectogen (System VI). The common feature observed in these binary phase diagrams is the stabilization of smectic, as well as, nematic phases, with one exception of system IV. This is due to the short alkoxy chain present in both of the components and such behaviour of binary systems is explained in the foregoing discussion. In the case of systems V and VI, alkyl as well as alkoxy chain length is increased which justifies the stabilized smectic phases in binary systems.[12] The study has provided many mixtures with wide ranges of mesophases. It also has highlighted that small changes in a component of binary mixture affect the mesogenic tendency of binary phase diagrams markedly.

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