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Mixed Mesomorphism-I: Determination of Latent Transition Temperatures (LTTs)

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ABSTRACT

Several binary systems have been studied by number of researchers consisting of one, none or both components as mesogenic; with a view to (I) understand the effect of structure on induction of smectic or/and nematic mesophase by mixing two components. (II) for its technological applications in which room temperature liquid crystals or wider temperature range liquid crystals are to be used. Eight binary systems consisting of none of the mesogenic component (A), n-alkyl-p-(p'-n-butoxy benzoyloxy) benzoate (Methyl & Ethyl) as common component and other Schiff's bases (B) are studied. Interesting results are obtained as, (1) Smectic or/and nematic mesophase are induced enantiotropically and monotropically. (2) Smectic and nematic mesophase are induced for binary system comprising monotropic nematic component (B). (3) Polarity of terminal groups, aromaticity and polarizability of component (A&B) play an important role in enhancing the liquid crystallinity. Latent transition temperatures of components consisting of binary system for smectic or/and nematic mesophases are determined, by extrapolation method. Results are agreed with each other and previous work with variation of 10º C-15º C. Transition temperatures were carefully observed through hot stage polarizing microscope.

Keywords: - Liquid crystal, Smectic, Nematic, Mesogen, Mixed Mesomorphism.

INTRODUCTION

Synthesis of pure liquid crystal material is not enough but study of binary systems is also definitely necessary in order to get LCD material of certain range of temperature and composition. Several binary systems have been studied earlier [1-5] with a view to understand the effect of terminal groups on liquid crystallinity in a mixed melt and to determine latent transition temperatures (LTTs) of components (A&B). Eight binary systems consisting of none of the

mesogenic component (A), and other component Schiff's bases (B) are studied. Transition temperatures are observed through hot stage polarizing microscope.

MATERIALS AND METHODS

(I) Preparation of components:

Component (A), n-alkyl-p-(p'-n-butoxy benzoyloxy) benzoate (Methyl & Ethyl) was prepared by usual established method [6, 7] and finally obtained in pure form. Binary mixtures were carefully prepared with maintainance of their homogeneity. Schiff's bases were prepared by refluxing equimolar amounts of corresponding aldehydes and amines in alcohol on a water-bath and recrystallised from alcohol. Melting points and transition temperatures are in good accordance with reported earlier [7].

(II) Preparation of Binary mixtures:

Binary mixtures were prepared by weighing accurately constituent components in known proportion. The binary mixtures were melted and thoroughly mixed till the mass appeared to be homogeneous. Homogeneous solid mass was ground and thin film of a sample was used for microscopic observation.

RESULTS AND DISCUSSION

Microscopic observations were plotted as transition temperatures versus the mole % of component (A) and phase diagrams are represented in the Table 1 & 2 and Figure-1 to 8 respectively. Mesomorphic - isotropic transition temperatures are extrapolated to zero mole % of (A) or/and (B) and LTT of nonmesogenic components are predicted. These values of LTT are well compared with each other & previous work with 5º c to 10º c variation. The geometry of the constituent components and the terminal or lateral groups attached to molecular structure of constituents components caused intermolecular attractions to such a magnitude that homogeneous mixture generates mesophase viz. nematic and/or smectic type at definite temperature enantiotropically or monotropically. Intermolecular forces of attraction happen to be capable of keeping molecules together with maintainance of parallel orientations or layered structure even in the floating condition. The composition and temperature range over which mesophase appears depend upon the degree of similarity of constituent components (A and B) of a binary system in size and shape, polarity of terminal groups, aromaticity and polarizability, The constituent component of binary systems are elongated lath like and similarities in geometry except the central bridge. Hence, considerable cohesive intermolecular forces of attractions conducive to mesophase formation operate over wider range of composition as shown in Table 3 & 4.

The minimum proportion of composition to disrupt completely the mesomorphic alignments of component (A_1) in a mixed melt are 68.7, 92.5 91.9, 92.33 mole% of B_1, B_2, B_3, B_4 respectively, for nematic or/and smectic mesophase. Thus disruption caused by nonmesogenic components B_1, B_2, B_3, and B_4 is in the expected order of the polarity of terminal groups. Schiff's base (3) shows nematic mesophase persistence over entire range of composition because component B_3 itself is monotropic nematic. But smectic mesophase is induced between 7.9 to 100 mole % of (A_1), This is because of the polarity of $-C_2H_5$ terminal group being more compared as to $-CH_3$ and -Cl terminal groups at the right(Y), keeping $-OCH_3$ terminal unchanged at the left(X), The minimum

proportion of composition require to disrupt entire the mesomorphic alignments of component (A_2) in a mixed melt are 50.4, 92.8, 84.3, 92.7 mole% of B_5, B_6, B_7, B_8 respectively for nematic and/or smectic mesophase. For binary system 3 and 7, nematic mesophase is exhibited over entire range of composition but smectic mesophase is induced between 7.9 to 100 mole% of(A_1) and for A_2 smectic mesophase is induced between 15.7 to 42.7%.This difference may be due to the difference of melting points of A_1 and A_2.For binary system 4 and 8, it is also seen that smectic mesophase is displayed between 7.67 to 87.5 and nematic mesophase is displayed between 63.5 to 87.0 mole % of A1, But for binary system 8 smectic mesophase is displayed between 7.3 to 23.5 mole % of A2 and nematic mesophase is completely absent. This is due to the difference in melting points of A1 and A_2.

The constituent components of all eight binary systems are geometrically rod like and structurally resemble each other. So polarizability of aromatic rings due to π-electron system, permitting conjugative interactions and terminal polarity of end groups of rod shaped molecules in which dipole moment acting across the long molecular axis in a mixed melt give rise to strong intermolecular attraction which are anisotropic and shows stability of the ordered arrangement of the molecules.

In case of binary system 2, 3, 4, 6, 7 nematic mesophase appears along with smectic mesophase. This suggests that, parallel alignment of the molecules are also maintained even in the floating condition of mixed melt even after the disruption of smectic mesophase i.e. even after the disruption of layered arrangement of molecules, the intermolecular cohesive forces are capable enough to maintain parallel orientation of molecules in a mixed melt as a result if the effect due to terminal groups of schiff's bases.

The mole% of component (A) are plotted versus the transition temperatures. The curves of the nematic isotropic transition temperatures or vice versa and smectic nematic transition temperature or vice versa in phase diagrams of binary systems(fig1 to 8) are extrapolated 0.0 mole % of A or/and B. Latent transition temperatures determined from phase diagrams are recorded in Table 5.

The LTTs for nematic and smectic mesophases are determined indicating potential of molecules to exhibit nematic or smectic mesophase. The LTT of component (A) is determined for smectic and nematic mesophase formation by extrapolating smectic-isotropic transition curve to 100 mole% of (A) respectively.

From table 5, it is clear that LTT predicted for schiff's bases 1,2,3,4 shows concurrency with very minor difference for A_1 and A_2.

LTT predicted for common component A_1 agrees well from phase diagrams of binary system of the type-1 within the difference of about 16.0ºC i.e. From 104.0ºC to 120.0ºC for smectic.

Similarly LTT for common component A_2 also well agrees within the difference of 14.0ºC i.e. from 61.0ºC to 75.0ºC for smectic and within difference of only 2ºC for nematic.

Table – 1: Transition temperatures in ^{o}C of Binary Systems( ) Values in parenthesis indicate monotropy.

	Component (B) X-C_6H_4-CH=N-C_6H_4-Y		Mole % of Component A_1											Eutectic point		Triple point	
	X	Y	Type of Mesophase	0	10	20	30	40	50	60	70	80	90	100	Temp. ^{o}C	Mole %	Temp. ^{o}C	Mole %
1	-OCH_3	-H	Smectic	-	-	-	50.0	50.0	52.0	59.0	68.0	80.0	-	-	50.0	40.0	-	-
			Nematic	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
			Isotropic	52.0	51.0	50.0	82.0	85.0	92.0	98.0	104.0	108.0	97.0	124.0	-	-	-	-
2	-OCH_3	-CH_3	Smectic	-	-	-	79.0	78.0	75.0	73.0	72.0	72.0	79.0	-	72.0	73.28	-	-
			Nematic	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
			Isotropic	91.0	92.0	84.0	92.0	96.0	99.0	103.0	106.0	108.0	110.0	124.0	80.0	22.7	-	-
3	-OCH_3	-OCH_3	Smectic	-	-	-	-	88.0	-	-	-	-	-	-	83.0	42.3	-	-
			Nematic	-	99.0	96.0	97.0	104.0	100.0	100.0	80.0	77.0	84.0	-	-	-	-	-
			Isotropic	147.0	138.0	135.0	130.0	125.0	117.0	110.0	108.0	110.0	115.0	124.0	76.0	74.61	-	-
4	-OCH_3	OC_2H_5	Smectic	-	98.0	87.0	80.0	70.0	70.0	69.0	68.0	70.0	80.0	-	68.0	43.73	-	-
			Nematic	(121.5)	118.0	114.0	105.0	94.0	84.0	81.0	81.0	87.0	97.0	-	-	-	-	-
			Isotropic	128.5	132.0	122.0	114.0	106.0	100.0	101.0	108.0	111.0	107.0	124.0	-	-	-	-
5	-OCH_3	-Cl	Smectic	-	(79.0)	(78.0)	(74.0)	76.0	70.0	68.0	(58.0)	(58.0)	(66.0)	-	68.0	60.0	81.0	36.0
			Nematic	-	-	-	-	-	-	-	70.0	78.0	92.0	-	-	-	78.0	62.5
			Isotropic	93.0	86.0	84.0	84.0	89.0	95.0	80.0	104.0	106.0	116.0	124.0	-	-	-	-

Table – 2: Transition temperatures in ^{o}C of Binary Systems ( ) Value in parenthesis indicates monotropy

	Component (B) X-C_6H_4-CH=N-C_6H_4-Y		Mole % of Component A_2											Eutectic point		Triple point	
	X	Y	Type of Mesophase	0	10	20	30	40	50	60	70	80	90	100	Temp. ^{o}C	Mole %	Temp. ^{o}C	Mole %
1	-OCH_3	-H	Smectic	-	-	39.0	40.0	40.0	40.0	42.0	44.0	49.0	64.0	-	39.0	20.0	-	-
			Nematic	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
			Isotropic	52.0	43.0	66.0	72.0	72.0	67.0	66.0	69.0	78.0	81.0	94.0	-	-	-	-
2	-OCH_3	-CH_3	Smectic	-	-	-	-	-	63.0	58.0	56.0	57.0	-	-	55.0	72.46	-	-
			Nematic	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
			Isotropic	91.0	93.0	89.0	82.0	71.0	68.0	68.0	73.0	74.0	73.0	94.0	-	-	-	-
3	-OCH_3	-OCH_3	Smectic	-	99.0	74.0	73.0	72.0	70.0	67.0	-	-	-	-	73.0	23.19	-	-
			Nematic	-	121.0	113.0	106.0	100.0	93.0	88.0	63.0	62.0	66.0	-	-	-	-	-
			Isotropic	147.0	145.0	144.0	137.0	127.0	116.0	105.0	94.0	84.0	77.0	94.0	61.0	78.0	-	-
4	-OCH_3	-OC_2H_5	Smectic	-	-	-	69.0	66.0	74.0	-	-	-	-	-	65.0	33.20	121.0	12.5
			Nematic	(121.5)	(115.0)	108.0	90.0	84.0	84.0	74.0	66.0	62.0	66.0	-	-	-	100.0	22.0
			Isotropic	128.5	125.0	120.0	117.0	111.0	103.0	93.0	84.0	78.0	74.0	94.0	62.0	74.88	-	-
5	-OCH_3	-Cl	Smectic	-	(70.0)	(68.0)	-	-	-	-	-	-	-	-	68.0	51.84	-	-
			Nematic	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
			Isotropic	93.0	91.0	82.0	74.0	71.0	68.0	74.0	81.0	86.0	90.0	94.0	-	-	-	-

Table –3

Sr. No.	Schiff Base (B) mixed with component (A_1)		Range of composition over which mesophase appears in terms of mole % of A_1
	X	Y	
1	$-OCH_3$	$-CH_3$	31.3 to 86.06 (Smectic)
2	$-OCH_3$	$-OCH_3$	33.8 to 42.3 (Smectic) 7.5 to 86.8 (Nematic)
3	$-OCH_3$	$-OC_2H_5$	7.9 to 87.50 (Smectic) 0.0 to 100.0 (Nematic)
4	$-OCH_3$	-Cl	7.67 to 81.5 (Smectic) 63.5 to 87.0 (Nematic)

Table – 4

Sr. No.	Schiff Base (B) mixed with component (A_2)		Range of composition over which mesophase appears in terms of mole % of A_2
	X	Y	
5	$-OCH_3$	$-CH_3$	49.6 to 85.5 (Smectic)
6	$-OCH_3$	$-OCH_3$	7.2 to 51.3 (Smectic) 7.2 to 86.4 (Nematic)
7	$-OCH_3$	$-OC_2H_5$	15.7 to 42.7 (Smectic) 0.0 to 100.0 (Nematic)
8	$-OCH_3$	-Cl	7.3 to 23.5 (Smectic)*

** indicate monotropy Smectic.*

Table - 5: LTT determined in ^oC

Schiff's base	LTT predicted in ^oC for			
	Type-1	Type-2	A_1	A_2
B_1	78.0 (Sm)	67.0 (Sm)	112.0 (Sm)	71.0 (Sm)
B_2	123.0 (Sm) 136.0 (Nm)	132.0 (Sm) 140.0 (Nm)	113.0 (Sm) -	61.0 (Sm) 75.0 (Nm)
B_3	118.0 (Sm) 121.5 (Nm)	120.5 (Sm) 121.5 (Nm)	120.0 (Sm)	74.0 (Sm)/(Nm)
B_4	60.0 - 74.0 (Sm)	74.0 (Sm)	104.0 (Sm) 116.0 (Nm)	73.0 (Sm)/(Nm)

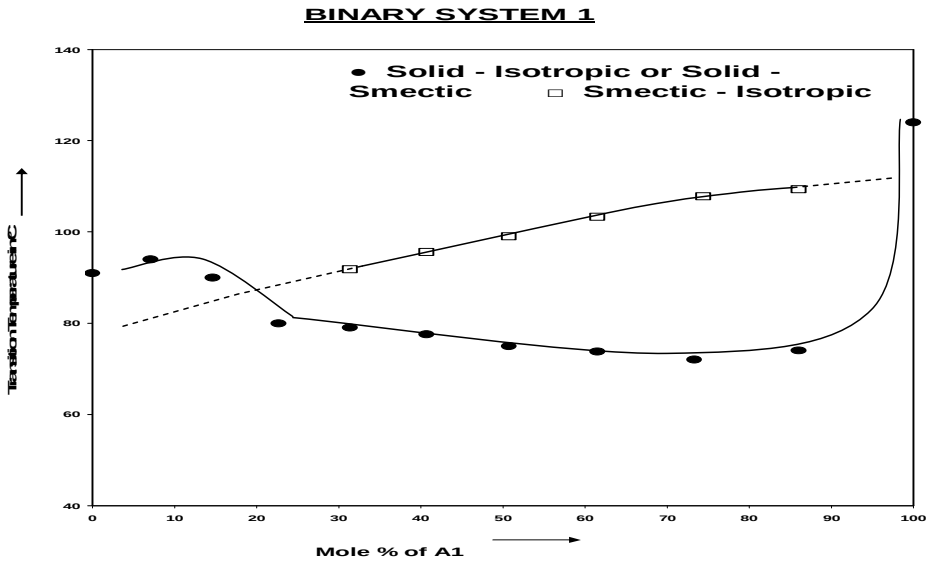
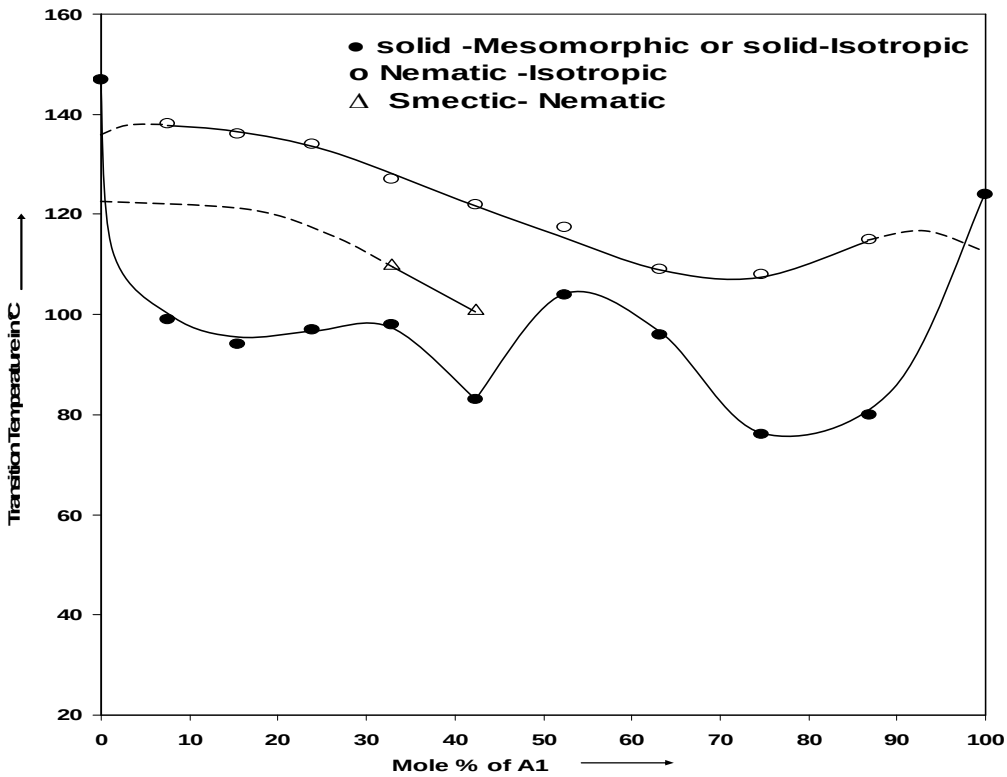


Figure 1. n-Methyl - p-(p'-n-butoxy benzoyloxy) benzoate. P-Anisal-p-Toluidine

Figure 2. n-Methyl - p-(p'-n-butoxy benzoyloxy) benzoate. P- Anisal - p - Anisidine



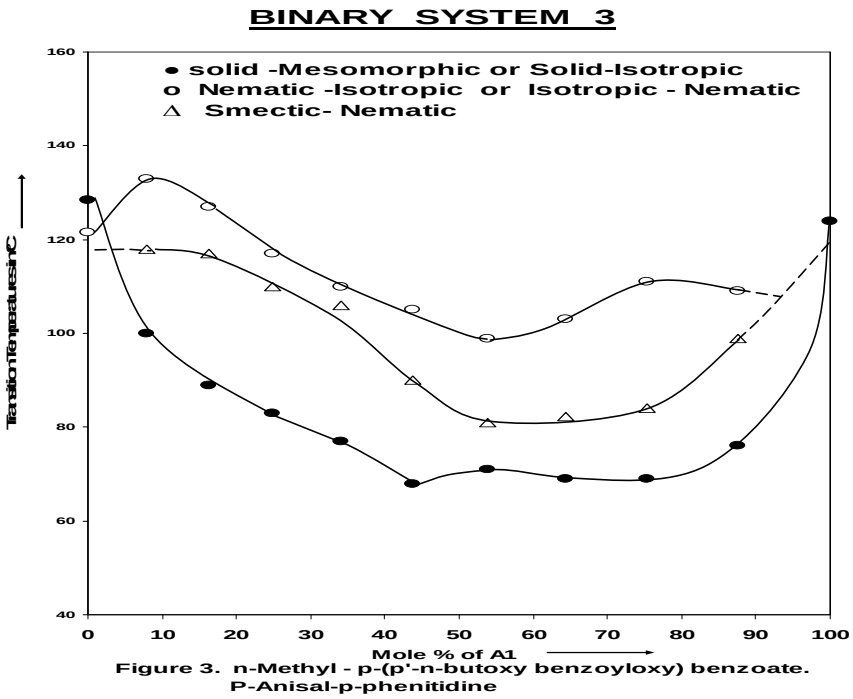


Figure 3. n-Methyl - p-(p'-n-butoxy benzoyloxy) benzoate.
P-Anisal-p-phenitidine

Figure 4. n-Methyl - p-(p'-n-butoxy benzoyloxy) benzoate.
P-Anisal-p-chloro Aniline

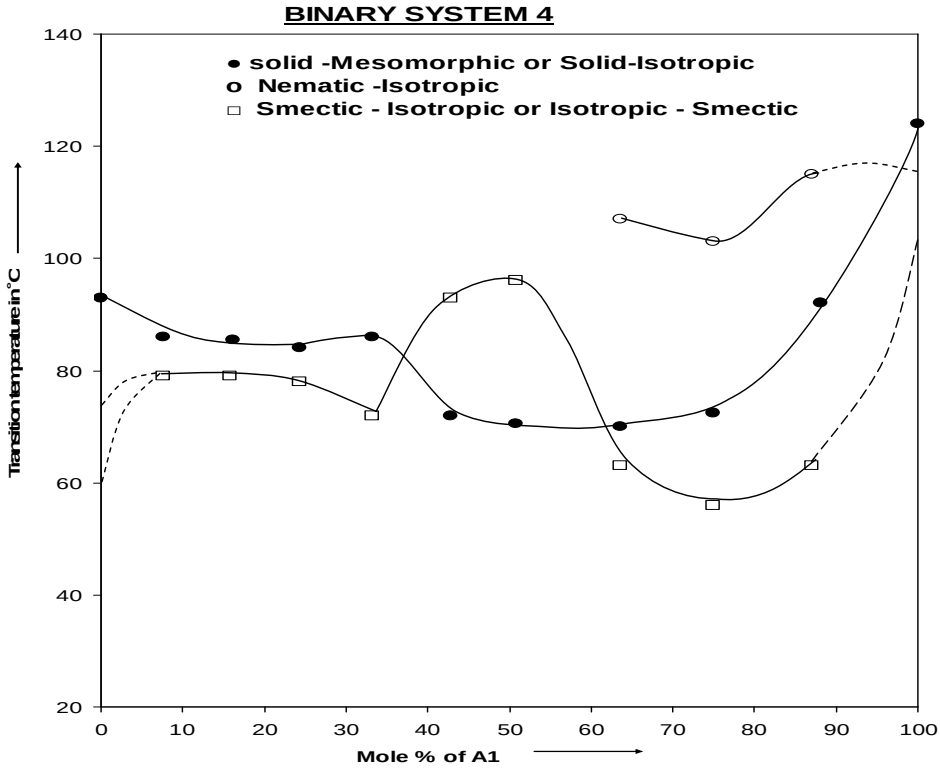
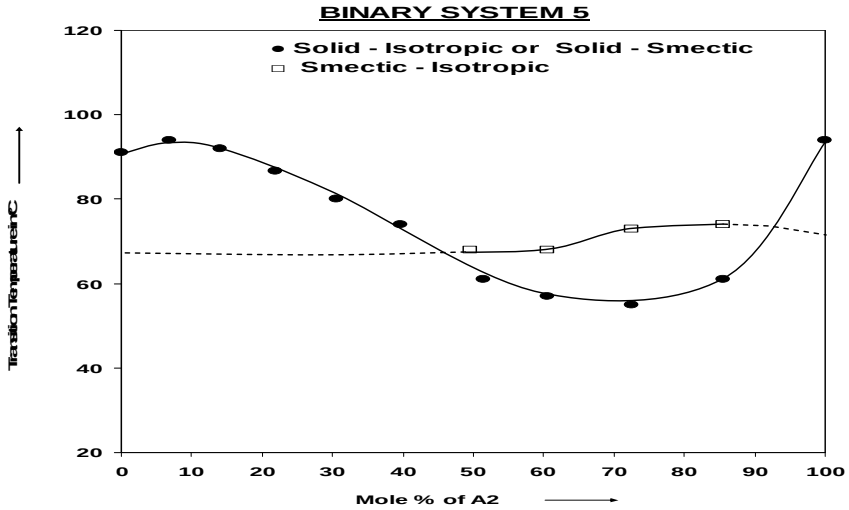


Figure 5. n-Ethyl - p-(p'-n-butoxy benzoyloxy) benzoate.
P-Anisal- p-toluidine



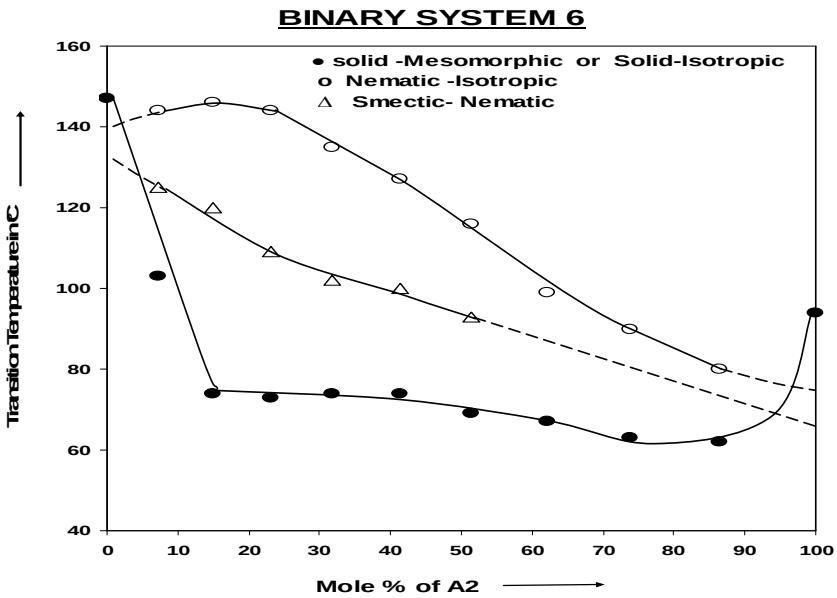


Figure 6. n-Ethyl - p-(p'-n-butoxy benzoyloxy) benzoate.
P-Anisal- p-Anisidine

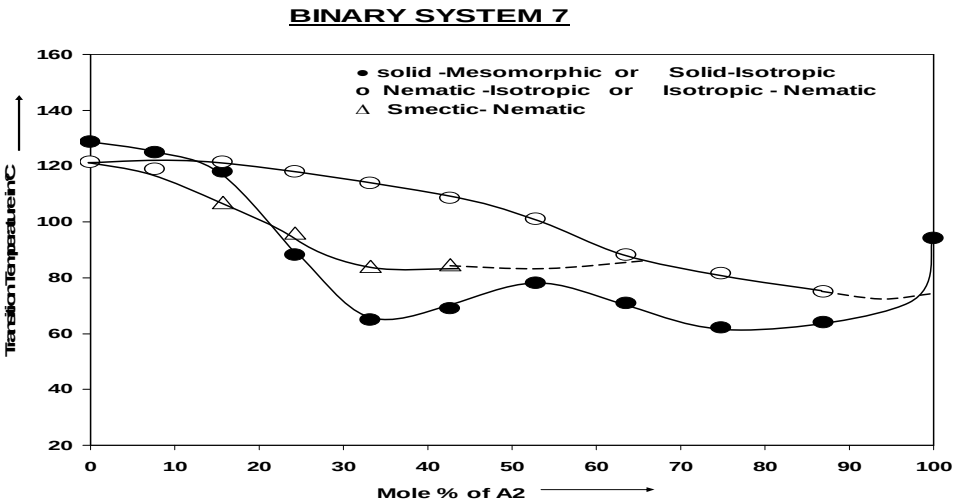


Figure 7. n-Ethyl - p-(p'-n-butoxy benzoyloxy) benzoate. P-Anisal- p-phenitidine

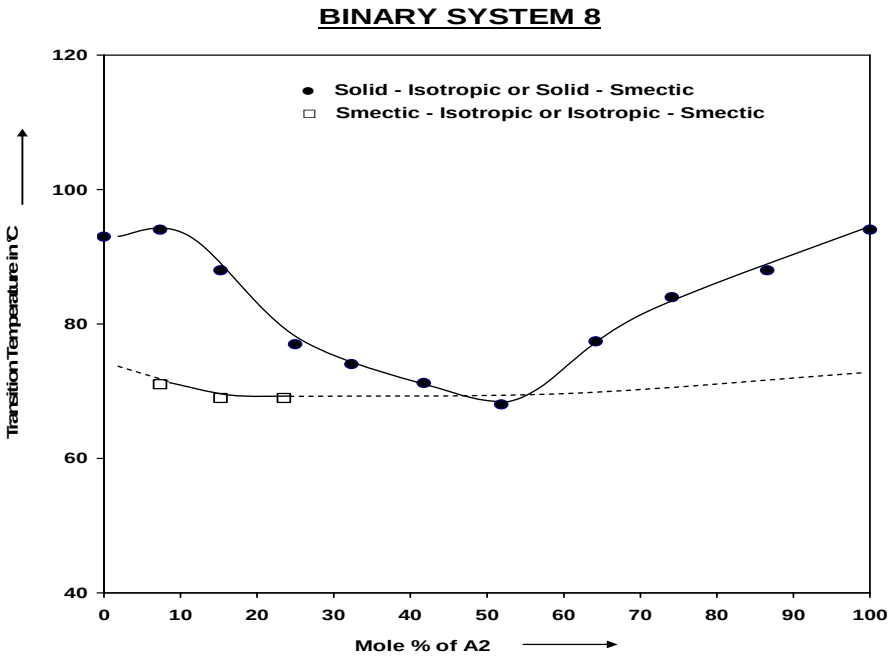


Figure 8. n-Ethyl - p-(p'-n-butoxy benzoyloxy) benzoate. P-Anisal- p-chloro Aniline

Thus credibility or reliability of the extrapolation method to determine LTT of nonmesomorphic component is placed on firm ground by present investigation.

Predicted LTTs for Schiff base component suggests that, a non mesomorphic or mesomorphic component can exhibit nematic and/or smectic type of property at a predicted temperature or within ±10.0ºC to 20.0ºC from predicted LTT, if it is supercooled suitably under proper experimental condition.

Thus every substance should have an intermediate state of matter, i.e. liquid crystalline state between crystalline solid and isotropic liquid but missing to display mesophase by any substances which may be due to not heated or supercooled at a suitable setting rate as required by the molecules, against to balance intermolecular attractions to maintain two dimensional layered arrangement of molecules or parallel alignment of molecules.

CONCLUSION

LTT determined by extrapolation of transition curve are well compared with each other. Thus reliability of determining LTT of nonmesogenic component by extrapolation method is further supported by present study.

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