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Effect of Molecular Structure on mesophase formation with Reference to Central group and the Determination of Latent Transition Temperature (LTT) by Extrapolation Method in Binary System

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ABSTRACT

Six binary system with three common Schiff's bases B_1, B_2, B_3 mixed with two different common components Viz. Trans p-[p′-methoxy cinnamoyloxy)anisole (A_1) [Nm 117.5°-141.5°] and p-Butyloxy benzal –p-chloro aniline [B_2] [Sm 85° - 91°C] of the binary systems were studied. Initial slop and hence "Group Slope" values and LTT were determined from the phase diagrams plotted for transition temperatures versus mole % of common component [A_1 or A_2]. Transition temperatures and melting points of pure components and the binary mixtures were observed through hot stage polarizing microscope. Components of binary systems were synthesized by usual established method and their analytical data matches very well with reported earlier. Though values of initial slopes and group slope differs, but group efficiency order and LTT values remains unaltered and matches with order and values reported earlier.

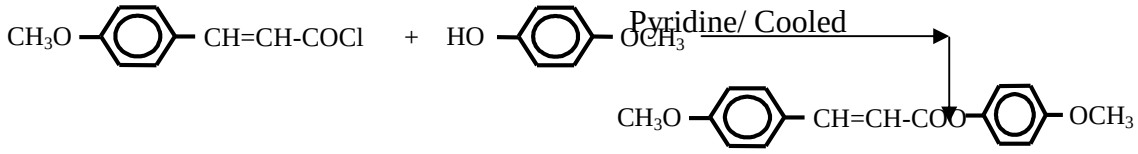
Keywords : Mixed Mesomorphism, Liquid crystals, Nematic, Smectic, Mixed melt.

INTRODUCTION

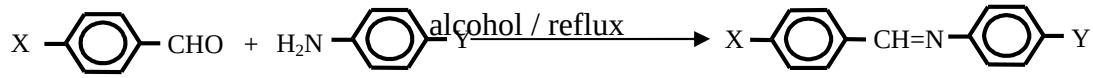
Several binary systems [1to 8] are studied by different researchers to study the effect of molecular structure and terminal end groups on Liquid Crystal phase formation, neglecting the effect and contribution of central bridge linking two phenyl rings. Present investigation is planned to study the contribution of central group on mixed mesophase formation and to check the reality of conclusions made by early workers about the effect and contribution of central group in the formation of mesophase in the mixed melt of a binary system and the determination of LTT of nonmesomorphs.

MATERIALS AND METHODS

Trans p-[p′-(methoxy cinnamoyloxy)]anisole [2] was prepared by reacting trans-p- methoxy chloride and p-hydroxy anisole in pyridine.



Schiff's bases A_2, B_1, B_2, B_3 were prepared [2] by reacting corresponding aldehyde with corresponding amine in alcohol.



Where, X = -OC_4H_9, -OC_2H_5 and Y= Cl, -CH_3, -OCH_3, -OC_2H_5

Materials

Anisaldehyde, p-Hydroxy anisole, Pyridine, Piperidine, Alcohol, p-Ethoxy bezaldehyde, p-Phenitidine, p-Anisidine, p-Toludine, p-Chloro aniline, p-Butyloxy bezaldehyde etc, were used as received.

Method: Binary mixtures were prepared by the method of Lohar and Doshi [2]. Melting and transition Temperatures were observed through hot stage polarizing microscope. Analytical data of pure components A_1, A_2, B_1, B_2, B_3 are in agreement with the structure of the molecules and their melting transition temperatures are matching with values reported earlier.

RESULTS AND DISCUSSION

Binary systems with varying central groups (-CH=CH-COO- and –CH=N-) and unchanged terminal groups are studied in order to confirm justify and support the general conclusions drawn earlier by Dave and Diwar , Dave and Lohar, Doshi et al about the effect of central group on mixed mesophase formation. Totally six binary systems consisting of nematogenic component A_1 and a smectogenic component A_2 as common component and Schiff's bases B_1, B_2, B_3, as second component of binary systems with $–OC_2H_5$ as common left (X) terminal and $–CH_3$, -OCH_3, and $–OC_2H_5$ as right (Y) terminal of Schiff's Bases B_1, B_2, B_3 respectively, were used. Therefore variation in liquid crystal properties depend only upon different central groups and the polarity of right terminals(Y) only, because anisotropic intermolecular forces of attractions of suitable magnitude arising out of these variation are responsible variation in liquid crystal properties, e.g. the extent of mole % range of component B_1, B_2, and B_3 of all the six binary systems over which mesophase exhibited, initial slopes and LTT determined with common components A_1 and A_2 are shown in table-1 as determined from phase diagrams shown in figure-1 and 2.

From table –1 the mole % of component B over which mesophase persisted are 82 ^{Nm}, 89^{Nm} and 90 ^{Nm} for binary system 1, 2 and 3 respectively and similarly for binary systems 4, 5 and 6 are 90 ^{Nm}, 90 ^{Nm} and 70 ^{Nm} + 31.5 ^{Sm} respectively. Such long or large mole % range over which mesophase observed facilate smooth and perceive trend of extrapolation of mesomorphic-isotropic (or vice versa) transition curve to determine and predict LTT of B_1, B_2 and B_3 because nematic-isotropic (or vice versa) transition curve meet the solid-isotropic or nematic transition curve to the left of the eutectic point i.e. Triple points are at the left of the eutectic point. On comparing the values of LTT determined for B_1, B_2 and B_3 are equal or equivalent and concurrent irrespective of variance in central groups viz –CH=CH-COO- and –CH=N-.

Moreover though initial slope values of transition curve considerably differs for group of binary systems A_1 +B_1, A_2 + B_1, A_1 + B_2, and A_2 + B_2, A_1 + B_3, A_2 + B_3 the group efficiency order derived for –CH_3, -OCH_3, and –OC_2H_5 for nematic and smectic which remains unaltered and very well matches with the group efficiency order derived earlier. In present study of six binary systems the left terminals [X] of B_1, B_2, B_3 are common i.e. –OC_2H_5. Therefore initial slopes of each mesomorphic-isotropic transition curve can be directly linked to group efficiency order or order of polarity of terminal group (Y) of Schiff's bases B_1, B_2, B_3.Without calculating individual group slope values for each terminal end group (Y) based on "additive effect". [2]

Table-1: Data from phase diagram

Sr.No.	Binary System	Melting point of component (B) in °C	Mesophase exhibited in mole % of (B)	LTT determined in °C	Initial Slope of Meso.-Isotropic transition curve °C/(mole %) x 10
*	A_1	Nm 117.5-141.5	-	-	-
1	A_1 +B_1	99.0	82.0	80.0 Nm B_1	8.0 Nm
2	A_1 + B_2	115.0	89.0	111.0 Nm B_2	6.5 Nm
3	A_1 + B_3	140.0	90.0	135.0 Nm B_3	5.0 Nm
*	A_2	Sm 85-91	-	98.0 – 100.0Nm	-
4	A_2 + B_1	99.0	90.0	80.0 Nm B_1	-4.0 Sm +3.0 Nm
5	A_2 + B_2	115.0	90.0	110.0 Nm B_2	- 2.5 Sm +2.0 Nm
6	A_2 + B_3	140.0	70.0Nm 31.5 Sm	135 Nm B_3	-5.0 Sm -9.0 Nm

Thus, group efficiency order derived on the bases of present investigation i.e. range of exhibition of present crystallinity or initial slope value or group slope value or the polarity of terminal end group (Y) for mesophase formation is as under.

$-OC_2H_5 > -OCH_3 > -CH_3$

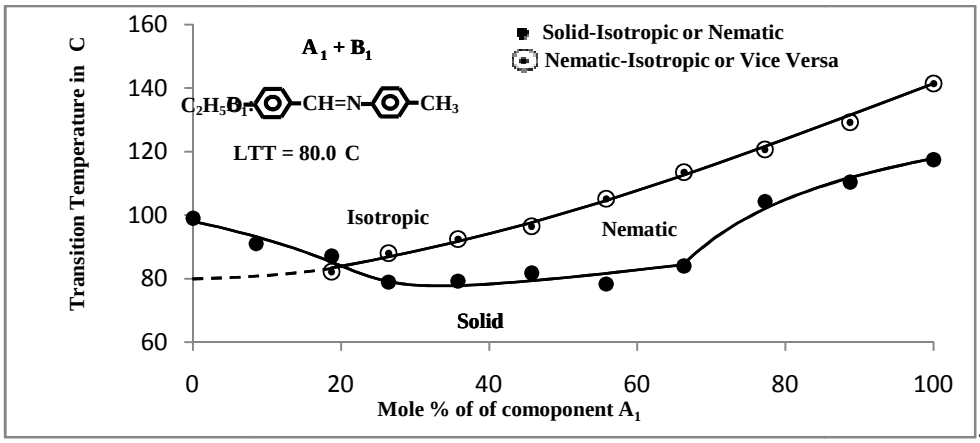
Table-2 Representative table of compositions and transition temperatures for Binary Systems A_1+B_1 and A_2+B_1

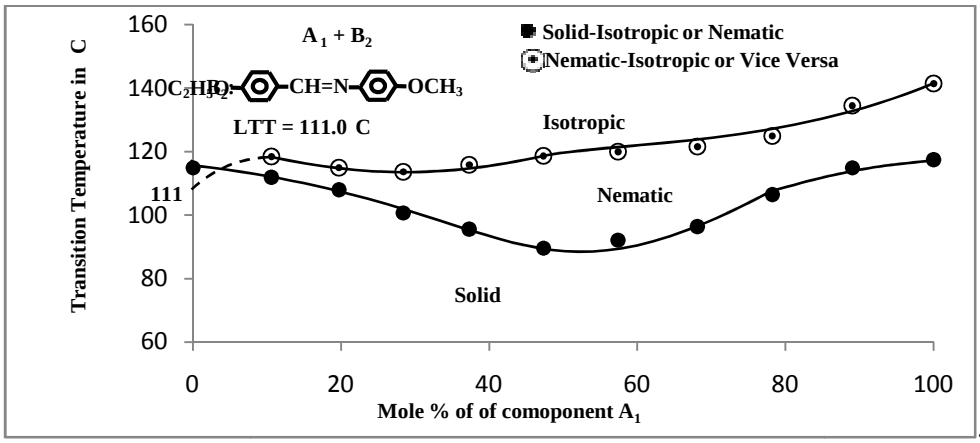
Sr.No	Binary System A_1 + B_1				Binary System A_2 + B_1			
	Composition in mole % of A_1	Transition Temp.			Composition in mole % of A_2	Transition Temp.		
		Sm	Nm	Iso.		Sm	Nm	Iso.
1	0.00	-	-	99.0	0.00	-	-	99.0
2	8.516	-	-	91.1	10.024	-	(80.7)	95.1
3	18.735	-	(82.2)	87.1	17.468	-	(80.9)	86.3
4	26.448	-	79.0	88.0	26.263	-	77.7	81.4
5	35.806	-	79.3	92.5	35.641	-	65.9	82.0
6	45.714	-	81.8	96.5	45.855	-	65.6	83.7
7	55.820	-	78.4	105.2	55.467	-	69.3	85.3
8	66.307	-	84.0	113.6	66.667	-	78.5	86.7
9	77.198	-	104.4	120.7	77.008	-	83.8	89.3
10	88.736	-	110.4	129.3	88.418	-	88.8	95.8
11	100.00	-	117.5	141.5	100.00	85.0	-	91.0

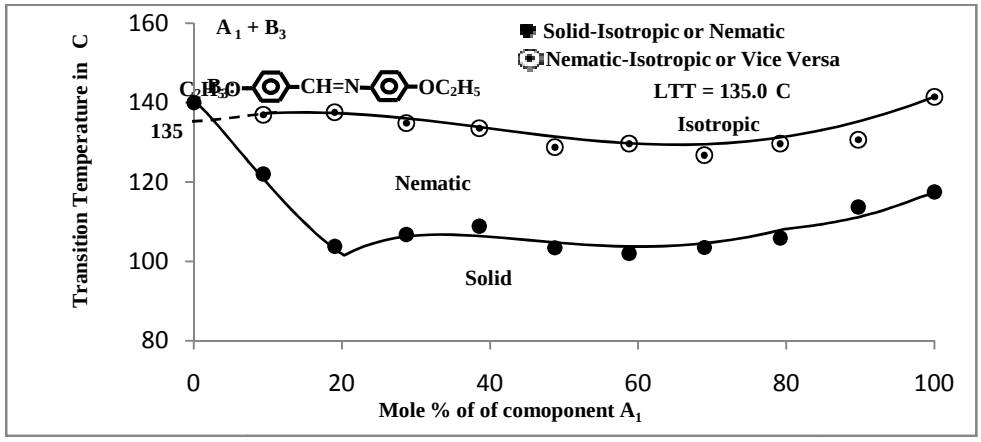
- *Value in bracket indicate monotropy*

Greater the 'group slope' value, proper is the efficiency of mesophase formation. This order of group efficiency of present study very well support the earlier conclusions [2 to 7]. The values of LTT and range of composition over which mesophase formation take place leads to the

conclusion that irrespective of any central group, order of polarity of terminal groups plays an important role and majorly contributes to the mesophase formation in the mixed melt of a binary system. Therefore the effect and contribution of a central group is negligibly small as suggested by early workers [2,3,8]. Thus present study very well support the early conclusions and puts polarity concept of mesophase formation on sound bases [1, 3, 7, 8]. Representative tables of two binary systems are given as Table-2.







CONCLUSION

The effect and contribution of central group in mesophase formation of a binary system is negligibly small, though initial slope of mesomorphic-isotropic transition curve or group slope value vary with the central and terminal groups.

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