



Scholars Research Library

Der Pharma Chemica, 2012, 4 (1):523-528
(<http://derpharmachemica.com/archive.html>)



ISSN 0975-413X
CODEN (USA): PCHHAX

Study of Binary Systems: Structural Relation with Mesophase and Determination of Latent Transition Temperature [L.T.T] of Nonliquid Crystal Schiff's Bases by Extrapolation Method.

Doshi A. V.*, Vyas N. N^a and Chauhan M. L.^b

*Matushri Virbaima Mahila Science & Home Science College, Rajkot (Gujarat-India)
^{a,b}Sheth P. T. Arts & Science College, Godhra(Gujarat, India)

ABSTRACT

Eight binary systems consisted of a common smectogenic component (A) *p*-butyloxy benzal -*p*-chloro aniline [85°C - 91°C] mixed with mesomorphic Schiff's bases B₁, B₂, B₃,.....B₈. A curve of a phase diagrams drawn from the transition temperatures, determined by the hot stage polarizing microscope versus mole % of component A is extrapolated to zero or 100 mole % of B to determine LTT of either of the component of a binary system. Encouraging results are obtained. Present work was planned to determine LTT of uncommon components B₁ to B₈ and to understand and establish the effect of terminal end groups on liquid crystal behaviour of Schiff's bases (B). Binary system A + B₈ does not show any sort of liquid crystal behaviour, Transition temperatures and LTT of pure components very well matches with the values reported earlier.

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

INTRODUCTION

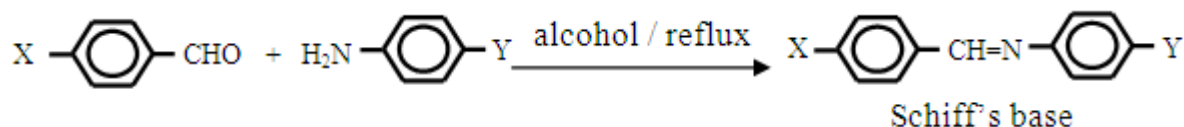
Several binary systems consisting of one none or both components liquid crystal have been studied earlier. Practically some substances exhibit liquid crystal mesophase in addition to well-known three states viz solid, liquid and gas. Presently, eight binary systems are planed to study with a view to understand effect of molecular structure on liquid crystal property and to predict latent transition temperature [LTT] for nonliquid crystal components with a latent ability to exhibit liquid crystal behaviour on the basis of extrapolation of the mesomorphic – isotropic (or vice versa) transition curve. Naturally, a search for their virtual transition temperature thus acquires importance.

MATERIALS AND METHODS

p-Butyloxy benzaldehyde [9] and *p*- Ethoxy benzaldehyde were synthesized by the method of Gray G. W. and Jones [1] from *p* – hydroxy bezaldehyde. *p*-Methoxy bezaldehyde or other

aldehydes and amines used to synthesize Schiff's bases, acetone, alkylhalide, K_2CO_3 ect. were used as received.

Schiff's bases were prepared by refluxing equimolar praportion [4] of corresponding aldehyde and amine in alcohol for three to four hours. Final products were purified in alcohol till constant transition temperatures obtained as reported in Table-1.



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

Binary mixtures were prepared by usual established method of Lohar and Doshi [2]. Transition temperatures and melting temperature of pure components and binary mixtures of binary systems were observed through hot stage polarizing microscope.

RESULTS AND DISCUSSION

Component (A) of binary system is p- Butyloxy benzal-p-chloro aniline with Smectogenic character enantiotropically between 85.0°C and 91.0°C . Uncommon components of Binary systems $A+B_1$, $A+B_2$ and $A+B_3$ have ethoxy group as a common left terminal [X] and $-CH_3$, $-OCH_3$, $-OC_2H_5$ as right terminal [Y] respectively. Component B_4 and B_5 bear $-CH_3$ as common left terminal [X] with $-OC_2H_5$ and $-OCH_3$ right terminal [Y] respectively. B_6 and B_8 components bear $-Cl$ as common left terminal [X] with varying $-OCH_3$ and $-Cl$ right terminal [Y] respectively, component B_7 contain $-OCH_3$ and $-CH_3$ as left [X] and right [Y] terminal end groups. Phase diagrams of all the binary systems were plotted for transition temperatures of a binary system versus the number of mole percent of component A. [Figure 1 to 8]. The mesomorphic-isotropic or vice versa transition curve is extrapolated to zero mole percent of component A to predict and determine LTT of component B_1 to B_7 . LTT determined for each Schiff's base are shown in table-1. Binary system $A+B_8$ does not show exhibition of liquid crystal behaviour because of the presence of weakly polar terminals $-Cl$ and $-Cl$ causing weaker and of low magnitude intermolecular forces of attractions which causes maximum disturbance in a mixed melt and molecules are failed to arrange themselves in two dimensional array in floating condition. Such molecules are randomly oriented with high magnitude of disorder without showing up of any sort of mesophase even in the monotropic condition. Binary systems $A+B_1$, $A+B_2$, $A+B_3$, $A+B_4$, $A+B_5$, $A+B_6$ and $A+B_7$ shows exhibition of liquid crystal behaviour within definite range of composition and temperature because, the molecules of B_1 to B_7 possess ability to pack into a single liquid crystal lattice and the favourable mean orientational cohesive energy density of the binary mixture in a mixed melt. The constituent components of binary system under present investigation are isodimensional [elongated] and of similar size, shape, aromaticity the steric factors are about the same for mixtures of all the composition, the orientational cohesive energy density vary more or less linearly with composition, following more or less law of ideal mixtures. Positive or negative deviation from ideal behaviour may be observed in transition line of a phase diagram, if the molecules of constituent components differ appreciably. As a result of this, the molecules of component A and B may face disturbance or difficulty in packing together. The entry of the molecules of component B into A, if fits in molecular arrangement, the mesomorphic-isotropic (or vice versa) transitions may rise or fall or liquid crystallinity may disappear depending upon extent of disturbing effect in molecular packing cinario. Disturbing effect is limited and it increases with increasing praportion of the component

(B). Thus a range of liquid crystal formation can be obtained, which is based upon the efficiency or polarity of terminal groups of component B and resistivity to bear disturbing effect of component A. Table-1 depicts the degree of liquid crystallinity exhibited in mole percent range of component B exhibited unhindered and LTT determined for each component B to arrive at their correlation with polarity of terminal end groups. Binary systems involving B₁, B₂ and B₃ in which presence of common left ethoxy terminal end group being more polar shows stronger intermolecular terminal attractions. In case of binary systems A+B₃ smectic and nematic mesophase formation occurs in a mixed melt. Right terminal end groups -CH₃ and -OCH₃ being less polar in binary systems A+B₁ and A+B₂ display only nematic mesophase over a considerable range of composition. In case of binary system A+B₁ overall polarity of -CH₃ terminal is comparable with terminal polarity of -Cl. Hence the liquid crystallinity exhibited is upto 90.0 mole % of component B₁. In case of binary systems A+B₄ and A+B₅ the extent of liquid crystallinity variation 92.5 and 83.5 mole % is attributed to polarity difference of -OC₂H₅ and -OCH₃ respectively. Binary systems A+B₅ and A+B₇ in which component B₅ and B₇ being isomeric and hence equipolar molecules, the overall liquid crystallinity exhibited 83.5 and 83.0 mole % of B due to 'additive effect' of two terminal groups. These two figures are quite in agreement. The replacement of -CH₃ by -Cl in binary system A+B₆, though -Cl and -CH₃ are equipolar but liquid crystallinity persisted upto 64.0 mole % in comparison with B₅. This difference in B₆ and B₅ is attributed to the difference of their melting points by 123.5-88.0 = 35.5°C. Thus disturbance caused by Schiff base B₈ i.e. p-Chlorobenzal p-chloroaniline is maximum in a binary system A+B₈.

Thus, Group efficiency order for nematic mesophase formation in terms of molecular polarity or functional group polarity or in terms of mole percent over which mesophase persistence can be derived as under.

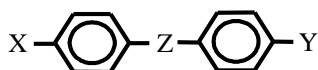
: With common -OC₂H₅ left terminal : -Cl > -CH₃ = -OCH₃ > -OC₂H₅

: With common -CH₃ left terminal group : -OC₂H₅ > -OCH₃

: With common -Cl left terminal group: -OCH₃ > -Cl

LTT determined by extrapolation mesomorphic – isotropic (or vice versa) transition curve in the each phase diagrams are reliable and comparable with the earlier study [5,6,7,8] for all the nonliquid crystal Schiff's base B₁ to B₇ under present investigation. Such reliability of LTT can be attributed to the meeting of the mesomorphic – isotropic (or vice versa) transition curve to solid – isotropic liquid curves to the left of the corresponding eutectic points. i.e. triple points are to the left of the eutectic point, which results into formation of mixed liquid crystal area maximum in a phase diagram and low value of the slope of the mesomorphic – isotropic transition curve with high degree of liquid crystallinity as a consequence of high polarity of terminal end groups. Component B of a binary system A+B₈ does not show any liquid crystal property. Hence the determination of LTT for p-Chlorobenzal p-chloroaniline [B₈] is ruled out. Table-1 represent LTT values determined presently and their comparison with earlier work [5,6,7,8]. Thus, present investigation is in good agreement with earlier work and hence very well support the conclusions drawn earlier. Also it raises the credibility of extrapolation method to determine LTT of nonliquid crystal substances. Table-2 represents the transition temperatures of two representative binary systems. Figure 1- represents phase diagrams of all the binary systems under present investigation.

Table-1 Schiff's Base: Component A mixed with component B [B₁ to B₈] with terminal groups X and Y central group Z [-CH=N-]



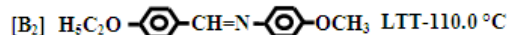
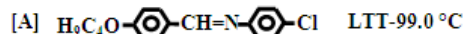
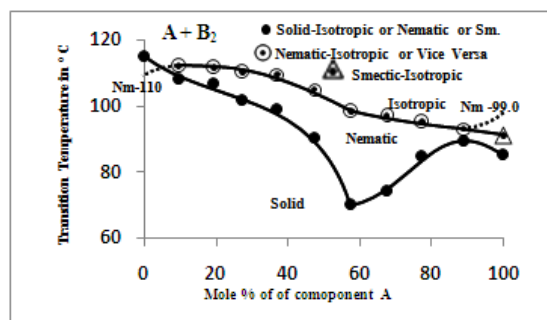
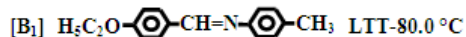
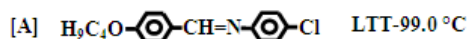
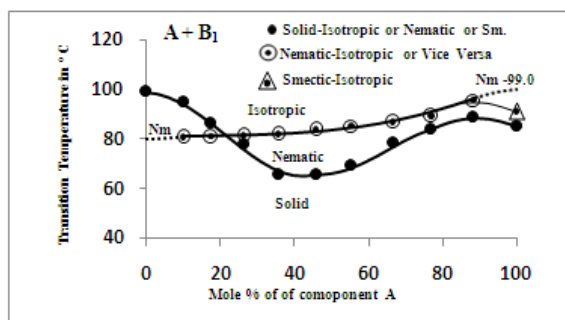
Component	X	Y	°C, Melting Point/ Transition point	Mesophase exhibited in mole % of B	LTT in °C Nematic			
					Determined present work (98-100) Nematic	I	II	III
A	-OC ₄ H ₉	-Cl	Sm 85-91 Iso.	-	(98-100) Nematic	-	-	-
B1	-OC ₂ H ₅	-CH ₃	99.0	90.0	80.0 Nm	80.0 Nm	-	-
B2	-OC ₂ H ₅	-OCH ₃	115.0	90.0	110.0 Nm	112.0	113.0	-
B3	-OC ₂ H ₅	-OC ₂ H ₅	140.0	70.0 Nm, 30.0 Sm	135.0 Nm	135.0	135.0	-
B4	-CH ₃	-OC ₂ H ₅	108.5	92.5	85.0 Nm	90.0	86.5	81.5
B5	-CH ₃	-OCH ₃	88.0	83.5	52.0 Nm	55.0	51.8	-
B6	-Cl	-OCH ₃	123.5	64.0	75.0 Nm	73.0	-	-
B7	-OCH ₃	-CH ₃	91.0	83.0	40.0 Nm	40.0	39.0	39.0
B8	-Cl	-Cl	112.0	00.00	-	-	-	-

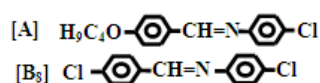
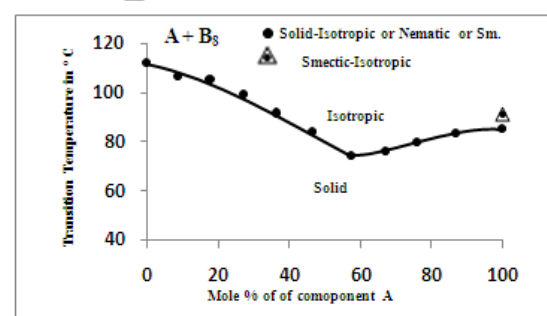
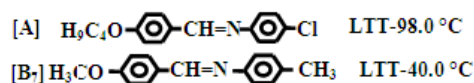
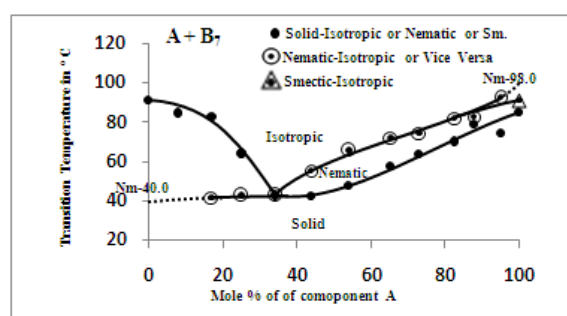
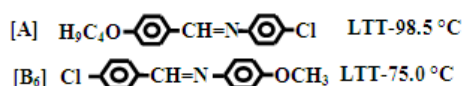
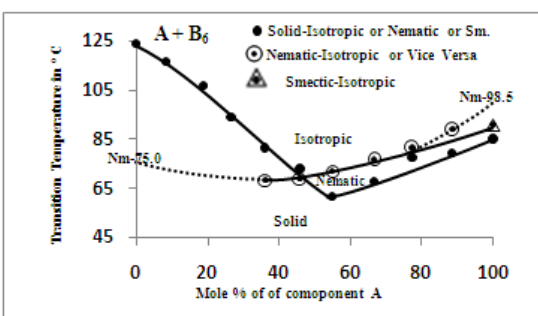
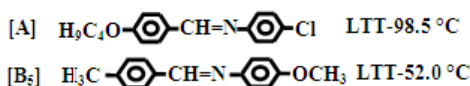
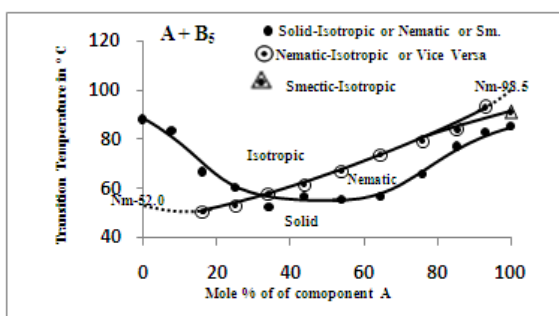
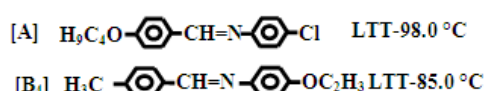
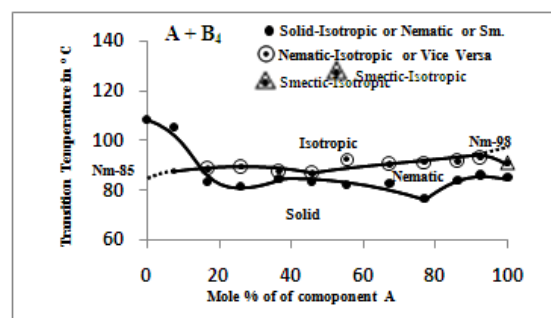
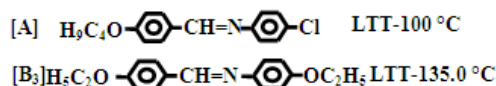
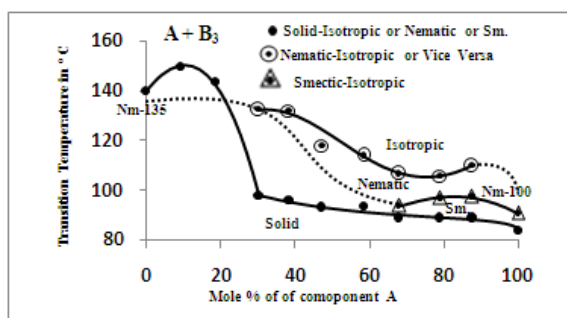
I, II, III other research workers [LTT in °C]

Table-2 Representative Tables of composition and Transition temperatures for Binary systems A+B₃ and A+B₅

Sr. No	Binary system A + B ₃				Binary system A + B ₅			
	Composition in mole % of A	Transition Temp.			Composition in mole % of A	Transition Temp.		
		Sm.	Nm.	Iso.		Sm.	Nm.	Iso.
1	0.0	-	-	140.0	0.00	-	-	88.0
2	9.239	-	-	149.5	7.834	-	-	83.5
3	18.649	-	-	143.6	16.273	-	(50.7)	66.6
4	30.245	-	97.7	132.5	25.060	-	(53.0)	60.3
5	38.398	-	95.8	132.0	34.321	-	52.5	58.0
6	47.268	-	93.3	118.0	43.797	-	56.5	61.6
7	58.427	-	93.5	114.0	54.026	-	55.5	67.0
8	67.877	91.0	92.6	106.6	64.628	-	56.4	73.8
9	78.977	91.3	95.4	105.9	75.956	-	65.6	79.3
10	87.675	91.0	96.2	110.0	85.519	-	77.0	83.8
11	100.0	85.0	-	91.0	100.0	85.0	-	91.0

Value in bracket indicate monotropy





CONCLUSION

- (1) Presence of strongly dipolar terminal end groups in a nonmesomorphic substance play the role to maintain statistically ordered parallel orientation or/and more ordered layered arrangement of the molecules to exhibit nematic or/and smectic mesophase formation in a mixed melt.
- (2) The polarity of terminal group is inversely proportional to molecular randomness or degree of molecular disorder in a mixed melt while, the melting point of a nonmesomorphic component [B] is directly proportional to molecular disorder or randomness or entropy of a system.
- (3)
- (4) Higher the polarity of a terminal end group, more is the probability of mesomorphic – isotropic (or vice versa) transition curve to meet the solid- isotropic transition curve to the left of the eutectic point. Such probability can be linked with the extrapolation of mesomorphic – isotropic transition curve.

Acknowledgement

Authors acknowledge thankful to the Applied chemistry dept., Fac. of Tech. & Engg., M.S. Uni. of Baroda, Vadodara for extending their valuable co-operation for allowing to carry out microscopic work.

REFERENCES

- [1] Gray G.W. and Jones B.J., *J. Chem. Soc.* 506, 1467 (1954)
- [2] A. V. Doshi and Lohar J. M. 1993 Proc. of Ind. Aca. of science, Bangalore Vol. 105, pp.-209- 214
- [3] Diwar MJS and Goldberg R. S. 1970 *J. Am. Chem. Soc.* 92 pp 1582
- [4] A. V. Doshi and N.N. Joshi, *J. Ind. Chem Soc.* Vol. 70. 1993 pp 807-809
- [5] A. V. Doshi and K. J. Ganatra *J. Ind. Chem Soc.* Vol. 77, 2000 pp 322-325
- [6] A. V. Doshi and N.G. Makwana *J. Ind. Chem. Soc.* Vol. 85, March 2008 pp. 262-266
- [7] A. V. Doshi and U. C. Bhoya and J. J. Travadi Paper presented and accepted and under Publication in coming volume of *Mol. Cryst. Liq. Cryst.* 2011.
- [8] Gray G. W. and Winsor P. A. *Liquid Crystal and Plastic Crystals*, Vol. 1, Ellis Harwood, John Willey and sons New York London-Sydney-Toronto chapter 5 and 4 P.P. – 287
- [9] A. V. Doshi and D. A. Odedare *J. Inst. of chemist (India)* 1993 Vol. 65 PP.158-160
- [10] V. R. Patel and A.V.Doshi, *Der Pharma Chemica* 2010 Vol. 2(6) PP. 429-436.