INFLUENCE OF MOLECULAR STRUCTURE ON LIQUID CRYSTALLINE PROPERTIES AND PHASE TRANSITIONS IN MIXED LIQUID CRYSTALS

BY

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Influence of Molecular Structure on Liquid Crystalline Properties and Phase Transitions in Mixed Liquid Crystals+

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Abstract - A number of binary systems comprising a liquid crystalline Schiff's base, viz. p-acetoxybenzal-p-phenetidine and a non-liquid crystalline Schiff's base are studied. In all these cases, the liquid phase, be it anisotropic or not, is a single homogeneous phase. There is no indication of two distinct liquid phases, one anisotropic and the other isotropic, coexisting side by side over a range of temperature, for a binary system of a given composition.

The shape of the transition lines in the phase diagrams of the binary mixtures is dependent on the type of the admixed non-mesomorphic component. In the case of systems comprising isomorphous components, the transition lines are almost linear. If the molecules of the two components differ in shape and size, owing to the difficulty in packing themselves together the transition lines of such binary systems exhibit a concavity. When the admixed component is altogether an odd molecule in shape, size and structure, compared to the mesomorphic component,

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the transition lines of such binary systems would be very steep, indicating the extremely little tendency of the odd non-mesomorphic component towards mixed mesomorphism.

The systems investigated here generally comprise isomorphous components. The slope of the transition line in these cases stands as a measure of the tendency of the non-liquid crystalline component to form mixed liquid crystals. The group slope values obtained from the slope of the transition lines are found to be additive and agree well with those obtained by Dave and Dewar[4] and Dave and Lohar[5] showing that the effect of the terminal groups is specific. The order of efficiency of the groups for mixed liquid crystal formation, in the present investigation, is as under :

$NO_2 > OC_2H_5 > OCH_3 > N(CH_3)_2 > CH_3 = Cl > Br$.

Mixed liquid crystal formation has been reported[1,2,3] in binary mixtures where one component is a nematic liquid crystal. Dave and Dewar[4] and Dave and Lohar[5] investigated the binary systems comprising p-azoxyanisole, a nematic liquid crystal and non-liquid crystalline Schiff's base compounds.

In the present investigation we have selected a Schiff's base, p-acetoxybenzal-p-phenetidine, another nematic liquid crystal and the mixed liquid crystal formation is studied in mixtures of this substance with non-liquid crystalline Schiff's bases.

Experimental :

Preparation and Purification of Materials :

The Schiff's bases are prepared by heating equimolecular proportions of corresponding aromatic aldehydes and amines, till condensation is ensured. The crude product is washed well with a suitable solvent like ethyl alcohol, benzene etc., and recrystallized into fine crystals which melt sharply.

p-Anisal-p-anisidine (148°), p-anisal-p-chloroaniline (92°), p-anisal-p-bromoaniline (120°), p-anisal-p-phenetidine (128.5°), p-anisal-p-toluidine (93°), p-dimethylaminobenzal-p-phenetidine (148°), p-nitrobenzal-p-chloroaniline (132°), p-chlorobenzal-p-phenetidine (122°), p-dimethylaminobenzal-p-bromoaniline (158°), p-chlorobenzal-p-anisidine (123.5°), p-nitrobenzal-p-phenetidine (123.5°), p-chlorobenzal-p-toluidine (128°) and p-nitrobenzal-p-bromoaniline (163°) were prepared and purified likewise ; their m.p.s agree with those recorded in the literature.

p-Ethoxybenzal-p-chloroaniline m.p. 100° (Found : N, 5.398. Requires N, 5.394), p-tolual-p-bromoaniline m.p. 125° (Found : N, 5.021. Requires N, 5.107), p-chlorobenzal-p-bromoaniline m.p.125° (Found: N, 4.729. Requires N, 4.754) and p-dimethylamino-benzal-p-chloroaniline, m.p. 152° (Found: N, 11.36. Requires N, 10.85).

Method of Study :

The phase diagrams are studied by the optical

and thermal methods[4].

Discussion :

A number of binary systems comprising a nematic liquid crystal, viz. p-acetoxybenzal-p-phenetidine and a non-liquid crystalline Schiff's base are studied. It is observed that there are no invariant lines in the phase diagrams of these binary systems, which imply that there are no two-phase liquid regions. Besides, the transitions from mesomorphic to isotropic liquid state were, in all cases, sharp and never took place over a range of temperature. This has been clearly supported by the breaks observed in the cooling curves of the mixtures (Fig.3) corresponding to such transitions, these being quite similar to the break observed in the cooling curve of pure p-acetoxybenzal-p-phenetidine.

Fig. 1. Phase diagram of p-Acetoxybenzal-p-phenetidine : p-Anisal-p-anisidine.

The mixtures were also studied on the Leitz Ortholux II polarizing microscope fitted with a heating stage. When the mixture on the slide is heated to isotropic liquid and cooled slowly, the transition from isotropic liquid to mesomorphic state could be marked clearly by the immediate appearance of nematic bubbles and similarly the crystallization from mesomorphic to solid state could also be observed. There is no indication of two liquid phases, one isotropic and the

other anisotropic, coexisting side by side. The transition from anisotropic state to isotropic is quite sharp and does not extend over a range of temperature for the binary mixture of a given composition. This shows that genuine mixed liquid crystals are obtained and that the anisotropic liquid phase is a single homogeneous phase of mixed liquid crystals.

Fig. 2. Phase diagram of p-Acetoxybenzal-p-phenetidine : p-Chlorobenzal-p-bromoaniline.

The shape of the transition lines in the phase diagrams of the binary mixtures changes depending on the type of the admixed non-mesomorphic component. In the case of binary systems comprising isomorphous components, the transition lines are almost linear. If the molecules of the two components differ in shape and size, owing to the difficulty in packing themselves together, the transition lines of such binary systems exhibit a concavity. When the admixed component is an odd molecule in shape, size and structure, compared to the mesomorphic component the transition lines in such binary systems would be very steep.

Fig. 3. A typical cooling curve of the system p-Acetoxybenzal-p-phenetidine (L.C) : p-Chlorobenzal-p-anisidine (N.L.C).

The systems investigated here, generally comprise

isomorphous components. Bogojawlensky and Winogradow[1] reported that in the case of isomorphous mixtures the transition lines are almost straight lines. Dave and Dewar[4] have, however, shown that in such systems the transition lines are not invariably straight and they can be curved to more or less extent. The transition lines of binary systems investigated here, are almost linear (see Figs. 1 and 2) and stand as a measure of the tendency of the non-mesomorphic component towards mixed mesomorphism. The lower the slope value, the greater is the tendency for the non-mesomorphic component to form mixed liquid crystals. The steep slope of the transition line indicates the low tendency of the non-mesomorphic component towards mixed mesomorphism. Table 1 gives the values of the slopes for the various substances studied here and the graphical observations of the study are recorded in Tables 4 and 5.

From Table 1 it can be seen that the slope values for isomeric pairs of Schiff's bases marked with an asterisk are similar. Further, the slope values vary with the polarity of the end groups and the effect is found to be additive.

The difference in slope values of the molecules having the same group at one end but different groups at the other end is almost the same. In the case of three such pairs cited in Table 2 the group slope difference is the same. Thus it is possible to deduce the group slope values for various terminal groups from the slopes

Table 1

Transition Line Slopes for the Compounds of the Type $R.C_6H_4.CH = N.C_6H_4.R'$ with p-Acetoxybenzal-p-phenetidine (in ^{o}C per 10 % change in molar composition)

Sys. No.	R	R'	Slope	Sys. No.	R	R'	Slope
1.	OCH_3	OCH_3	4.0	9.+	OC_2H_5	Cl	8.3
2.	+OCH_3	Cl	9.0	10.	NMe_2	Br	14.1
3.	OCH_3	Br	10.0	11.	CH_3	Br	15.75
4.	OCH_3	OC_2H_5	3.0	12.	Cl	Br	15.75
5.	OCH_3	CH_3	9.0	13.+	Cl	OCH_3	9.0
6.	NMe_2	OC_2H_5	6.5	14.	Cl	CH_3	14.5
7.	NO_2	Cl	7.8	15.	NO_2	Br	9.0
8.	+Cl	OC_2H_5	8.3	16.	NMe_2	Cl	12.8
				17.	NO_2	OC_2H_5	1.5

Table 2

Slopes for Various Schiff's bases

	R' =	OC_2H_5	Cl	Br
R =	NO_2	1.5	7.8	9.0
	NMe_2	6.5	12.8	14.1
Difference		5.0	5.0	5.1

Table 3

Group Slopes of Terminal Groups

	NO_2 >	OC_2H_5 >	OCH_3 >	NMe_2 >	Me =	Cl >	Br
Results of previous workers with p-azoxyanisole as liq. crystal.	0.5	1.1	2.6	5.6	7.2	7.2	8.9
Results of the present investigation.	0.5	1.0	2.0	5.6	7.2	7.2	8.5

of the transition lines. The terminal groups are arranged in an increasing order of efficiency towards mixed mesomorphism. The general order and their corresponding slope values obtained in the present investigation agree and compare well with those obtained by Dave and Dewar[4] and Dave and Lohar[5], with p-azoxyanisole as the liquid crystalline component (See Table 3).

The results suggest that the effect of the terminal groups is specific and should operate in binary mixtures of nematic liquid crystals with a non-liquid crystalline component, provided the two components are similar in shape, size and structure, and are conducive to close packing of the molecules in a given domain.

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Table 4

Solid-mesomorphic Temperatures for the Binary Systems. The Eutectic Temperatures and the m.p.s of Pure Components are Direct Experimental Values. The Other Temperatures were read from the Phase Diagrams.

Sys. No.	Component A with compound of the type $R.C_6H_4.CH:N.C_6H_4.R'$		Mole % p-acetoxybenzal-p-phenetidine (Component A)										Eutectic	
	R	R'	0	10	20	30	40	50	60	70	80	90	100	Mole % A	Temp. °C
1.	OCH_3	OCH_3	148.0	141.8	134.5	126.5	117.5	107.2	95.5	100.0	107.5	113.5	118.5	61.5	93.5
2.	OCH_3	Cl	92.0	86.2	80.5	74.8	69.0	73.5	82.5	91.5	100.5	109.5	118.5	43.0	67.5
3.	OCH_3	Br	120.0	112.5	105.0	97.2	89.8	86.0	91.2	97.0	103.4	110.5	118.5	47.0	84.0
4.	OCH_3	OC_2H_5	128.5	122.8	117.0	111.2	105.8	100.0	94.4	100.8	107.2	113.2	118.5	60.2	94.0
5.	OCH_3	CH_3	93.0	88.2	83.5	78.5	79.0	84.4	90.5	97.0	103.5	110.2	118.5	34.5	76.5
6.	NMe_2	OC_2H_5	148.0	142.0	136.8	131.5	126.0	129.0	113.8	106.5	105.0	110.0	118.5	74.0	103.5
7.	NO_2	Cl	132.0	123.6	115.5	107.8	100.5	93.8	87.0	89.0	98.5	108.2	118.5	64.5	83.5
8.	Cl	OC_2H_5	122.0	116.5	111.0	105.5	100.0	94.5	96.2	102.0	107.2	112.8	118.5	53.5	92.8

Table 4 (Contd.)

9.	OC_2H_5	Cl	100.0	95.0	90.0	85.0	81.0	86.0	91.4	97.0	103.5	110.8	118.5	39.0	80.2
10.	NMe_2	Br	158.0	151.8	145.5	139.0	132.6	125.2	117.0	108.0	107.0	110.0	118.5	73.5	105.0
11.	CH_3	Br	125.0	118.5	111.0	103.0	94.0	92.2	99.5	103.4	107.0	112.0	118.5	46.0	88.0
12.	Cl	Br	125.0	118.2	111.2	105.0	98.0	95.0	101.0	105.0	108.0	112.5	118.5	47.0	93.6
13.	Cl	OCH_3	123.5	116.0	108.6	101.4	94.0	86.5	88.0	97.5	105.8	112.5	118.5	55.0	82.5
14.	Cl	CH_3	128.0	120.2	112.5	105.0	97.5	91.0	97.5	101.0	105.5	111.5	118.5	49.5	90.0
15.	NO_2	Br	163.0	157.5	151.5	144.6	136.5	127.5	116.6	105.5	102.5	108.6	118.5	75.0	100.0
16.	NMe_2	Cl	152.0	146.5	140.2	133.5	125.8	118.0	110.0	102.5	104.0	111.0	118.5	74.0	99.5
17.	NO_2	OC_2H_5	123.5	117.5	110.8	103.4	95.5	86.5	89.2	96.5	104.0	111.2	118.5	52.5	83.5

Table 5

Mesomorphic-liquid Temperatures for the Binary Systems. The Values were read from the Phase Diagrams.

Sys. No.	Component A with compound of the type R.C_6H_4.CH: N.C_6H_4.R		Mole % p-acetoxybenzal-p-phenetidine (Component A)											Triple point	
	R	R'	0	10	20	30	40	50	60	70	80	90	100	Mole % A	Temp. °C
1.	OCH_3	OCH_3	-	-	--	-	-	115.5	120.0	124.4	128.8	133.2	137.5	44.5	113.2
2.	OCH_3	Cl	-	-	--	71.6	85.4	94.5	102.5	111.2	120.0	128.5	137.5	28.8	75.5
3.	OCH_3	Br	-	-	-	-	-	90.8	100.0	109.2	119.0	128.0	137.5	45.0	86.0
4.	OCH_3	OC_2H_5	-	-	121.6	123.0	124.5	126.0	127.8	129.5	132.0	134.5	137.5	13.8	121.0
5.	OCH_3	CH_3	-	-	-	-	86.4	95.0	103.2	111.8	120.2	128.5	137.5	30.8	78.2
6.	NMe_2	OC_2H_5	-	-	-	-	-	-	116.0	120.8	125.8	131.2	137.5	58.0	115.0
7.	NO_2	Cl	-	-	-	-	-	97.8	105.6	113.6	121.5	129.5	137.5	47.4	95.5
8.	Cl	OC_2H_5	-	-	-	-	107.5	111.5	115.5	119.0	123.8	129.5	137.5	32.0	104.5

Table 5 (Contd.)

9.	OC_2H_5	Cl	-	-	94.0	97.8	102.0	106.0	111.0	116.8	123.0	130.0	137.5	15.0	92.5
10.	NMe_2	Br	-	-	-	-	-	-	-	-	111.5	124.5	137.5	76.0	106.0
11.	CH_3	Br	-	-	-	-	-	-	-	-	108.8	121.8	137.5	78.0	106.0
12.	Cl	Br	-	-	-	-	-	-	-	-	-	122.0	137.5	81.0	109.0
13.	Cl	OCH_3	-	-	-	-	-	97.5	104.5	112.5	121.5	129.0	137.5	43.0	91.5
14.	Cl	CH_3	-	-	-	-	-	-	-	104.5	113.5	124.0	137.5	64.0	99.0
15.	NO_2	Br	-	-	-	-	-	-	-	107.0	117.0	127.5	137.5	69.5	106.2
16.	NMe_2	Cl	-	-	-	-	-	-	-	102.5	112.0	123.8	137.5	70.0	102.5
17.	NO_2	OC_2H_5	-	-	-	110.0	116.0	121.4	126.0	130.0	133.5	136.0	137.5	25.2	107.0

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MIXED MESOMORPHISM IN MIXTURES OF SCHIFF'S BASES

BY

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Fig. No. in the Paper	Fig. No. in the Thesis
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2	83
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4	85

Mixed Mesomorphism in Mixtures of Schiff's Bases

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ABSTRACT

Mixed liquid crystal formation has been studied in some binary mixtures comprising non-liquid crystalline Schiff's bases. Some of them are found to exhibit mixed mesomorphism over a certain range of temperature and concentration. The results are in agreement with the findings for a binary mixture of non-liquid crystalline components. For a binary mixture of chemically similar non-liquid crystalline components to exhibit mixed mesomorphism, the eutectic alongwith the mixed melting points of at least some compositions should fall below the mixed transition points of the crystalline liquid phase, which lie between the two latent transition temperatures of the pure components.

Bogojawlensky and Winogradow[1] studied the mixtures of isomorphous substances wherein one or both the components are non-mesomorphic by themselves and reported that mixed liquid crystals are obtained within a certain concentration region in either case. Walter[2] has also reported about the formation of mixed liquid crystals (MLC) in binary mixtures of non-mesomorphic components. Recently, Dave and Lohar[3] have reported mixed mesomorphism in mixtures of non-liquid crystalline

Schiff's bases. In the present paper results of similar studies with mixtures of a number of non-liquid crystalline Schiff's bases are reported. The four systems studied give mixed liquid crystals over a range of temperature and concentration.

Materials and Methods :

The four systems comprising non-liquid crystalline Schiff's bases studied were as follows :

System I : (A) p-nitrobenzal-p-anisidine +
(B) p-anisal-p-phenetidine

System II : (A) p-ethoxybenzal-p-phenetidine +
(B) p-dimethylaminobenzal-p-phenetidine

System III : (A) p-ethoxybenzal-p-phenetidine +
(B) p-anisal-p-phenetidine

System IV : (A) p-ethoxybenzal-p-phenetidine +
(B) p-nitrobenzal-p-phenetidine

The phase diagrams were plotted using the optical method[4].

Results and Discussion :

Mesomorphism in mixtures of Schiff's bases : Mixed liquid crystals formation : -

The mole per cent of components (A) in systems I - IV over which mixed liquid crystals are obtained is 38.5 - 51.5, 44.0 - 73.0, 21.0 - 59.0 and 27.5 - 82.5 respectively (Figs. 1 - 4). The range over which MLC are formed should normally vary with the overall

polarity of the end groups present in the binary system. System (IV) exhibits mixed mesomorphism over a larger concentration range while system (I) over a concentration range which is least of all. The range over which mixed mesomorphism is exhibited increases with overall efficiency of the system, contributed by the terminal groups present in the two non-liquid crystalline components. Therefore, in such systems the polarity alone cannot be taken as the only prerequisite for a binary mixture of non-liquid crystalline components to exhibit mixed mesomorphism for, many such binary systems possessing highly polar groups, fail to exhibit mixed mesomorphism. The virtual or latent transition temperatures in such cases are much below their normal melting points and no liquid crystalline phase is obtained.

Hence, it may be said in agreement with Walter, that for a binary mixture of chemically similar non-liquid crystalline components to exhibit mixed mesomorphism, the eutectic alongwith the mixed melting points of at least some compositions should fall below the mixed transition points of the crystalline liquid phase, which lie between the two latent transition temperatures of the pure components.

The latent transition temperatures of the non-liquid crystalline substances obtained by the extrapolation of the nematic-isotropic transition lines on either side in their mixtures exhibiting mixed

mesomorphism should agree with the corresponding values obtained by extrapolation of the transition lines of these non-mesomorphic substances separately with any liquid crystalline component of similar shape and structure. Such a comparison is given in Table 1.

Table 1

Comparison of the Latent Transition Temperatures of Non-Liquid Crystalline Components

Non-liquid crystalline component	LTP, °C., extrapolated in mixtures with	
	p-Acetoxy-benzal-p-phenetidine	Non-mesomorphic substances
p-Ethoxybenzal-p-phenetidine	143.0	143.0
p-Anisal-p-phenetidine	121.5	121.5
p-Dimethylaminobenzal-p-phenetidine	97.5	97.5
p-Nitrobenzal-p-phenetidine	84.5	85.0

The LTP's obtained for p-ethoxybenzal-p-phenetidine and p-anisal-p-phenetidine are 143.0 and 121.5 respectively and they agree with their corresponding monotropic mesomorphic temperatures in the literature[5-7]. These results indicate that a reliable extrapolation for deducing the latent transition

temperatures of the non-mesomorphic substances as suggested by Bogojawlensky and Winogradow[1] is possible, but it should be emphasized that the extrapolation will be reliable only in the case of binary mixtures having almost linear transition lines. On the other hand, if the admixed molecules are dissimilar, then the transition lines in such binary systems would be either steep or would exhibit a concavity ; in either case the extrapolation will not be possible.

Based on his studies of mixtures of isomorphous substances, Walter[2] suggested the Eq.(1) for the calculation of the transition points based on the Law of Mixtures.

$$t_m = (t_1C_1 + t_2C_2) : (C_1 + C_2) \quad \ldots\ldots (1)$$

where, t_m is the transition point of the mixed melt, t_1 and t_2 are the transition temperatures of the two components and C_1 and C_2 their concentrations in mole per cent. Eq. (1) can be applied where the transition points of the mixtures fall regularly between the two transition temperatures. The observed values of the transition points as well as the calculated values are given for few systems in Table 2. A little difference between the observed and the calculated values in some cases may be said to be due to the deviation of the actual transition curves from the hypothetical transition lines.

Bennett and Brynmor Jones[8] have shown that p-methoxybenzoic and p-ethoxybenzoic acids do not form

liquid crystals by themselves due to their high melting points, but formed nematic liquid crystals when the mixture of these two was melted as a result of lowering in their melting points. Lohar[9] confirmed these findings and showed that the mixture gives MLC over a small range of temperature and concentration. Walter[2] studied the systems containing p-methoxybenzoic and p-ethoxybenzoic acids separately in mixture with p-methoxycinnamic acid, a mesomorphic substance. By the extrapolation of the corresponding transition lines he determined the latent transition temperatures for both p-methoxybenzoic and p-ethoxybenzoic acids. During the course of the present investigation, the two acids were studied separately with another liquid crystalline component p-n-butoxy-benzoic acid and their latent transition temperatures determined by reliable extrapolation of almost linear transition lines in either case. The latent transition temperatures for these substances were also determined by Lohar[9] with p-methoxycinnamic acid as the liquid crystalline component. There is a close agreement between the values of the latent transition points (LTP) obtained in the present investigation when compared with those obtained by Walter[2] and Lohar[9] (Table 3).

It is thus clear that the LTP's could be reliably determined by extrapolation provided the mesomorphic and the non-mesomorphic components are isomorphous. This may be further supported by the fact

Table 2

Observed and Calculated Values of Transition Points for Various Systems Comprising Mixtures of Schiff's Bases

(A) p-Acetoxybenzal-p-phenetidine
(m.p. 118.5° ; TP 137.5°)

(B) p-Ethoxybenzal-p-phenetidine
(m.p. 148.0° ; TP 143.0°)

Mole % (B)	T.P.Obs.	T.P.Calc.
2.44	136.8	137.6
5.21	136.0	137.7
9.82	135.5	138.0
16.15	135.8	138.3
20.59	136.0	138.6
26.43	136.0	139.0
31.21	136.2	139.2
35.85	136.4	139.4
40.67	136.5	139.7
46.17	137.0	140.0
49.96	137.2	140.2
56.00	137.5	140.5
60.80	138.0	140.8
66.36	138.6	141.1
70.59	139.0	141.3
77.49	140.0	141.7
81.40	140.5	141.8
91.51	142.0+	142.5+
95.72	142.5+	142.7+

Table 2 (Contd.)

(A) p-Acetoxybenzal-p-phenetidine
(m.p. 118.5° ; TP 137.5°)

(B) p-Anisal-p-phenetidine
(m.p. 128.5° ; TP 121.5°)

Mole % (B)	T.P.Obs.	T.P.Calc.
6.04	136.0	136.5
11.33	134.0	135.6
16.84	133.0	134.8
21.80	131.0	134.0
26.87	130.0	133.2
31.69	129.0	132.1
37.21	128.0	131.5
42.23	127.0	130.7
48.26	126.0	129.7
52.35	125.5	129.1
62.29	124.0	127.5
71.52	123.0	126.0
80.55	122.0	124.6
90.46	121.0+	123.0+
93.91	121.2+	122.4+
96.98	121.4+	122.0+

Table 2 (Contd.)

(A) p-Ethoxybenzal-p-phenetidine
(m.p. 148.0° ; TP 143.0°)

(B) p-Anisal-p-phenetidine
(m.p. 128.5° ; TP 121.5°)

Mole % (B)	T.P.Obs.	T.P.Calc.
5.74	142.0+	141.7+
10.63	141.0+	140.6+
15.57	140.0+	139.6+
21.86	138.5+	138.3+
25.94	137.5+	137.4+
31.83	136.2+	136.1+
36.88	135.0+	135.0+
40.71	134.0+	134.2+
46.32	133.0	133.0
51.23	132.0	131.8
55.65	131.0	131.0
61.15	130.0	129.8
66.78	129.0	128.6
70.64	128.0	127.7
74.99	126.5	126.9
80.60	125.2+	125.6+
84.35	124.5+	124.7+
90.73	123.2+	123.5+

+ Values indicate monotropic mesomorphic temperatures.

Table 3

Comparison of Latent Transition Temperatures of p-Methoxybenzoic and p-Ethoxybenzoic acids

LTP, °C., extrapolated in mixtures with

Non-mesomorphic component	p-Methoxycinnamic acid (Lohar)	p-Methoxycinnamic acid (Walter)	Mixtures of alkoxybenzoic acids (Lohar)	p-n-Butoxybenzoic acid (present study)
p-Methoxybenzoic acid	157.5	155.6	156.5	155.5
p-Ethoxybenzoic acid	169.0	165.0	169.5	168.5

Captions :

Fig. 1 - Mixed liquid crystal formation in the system p-nitrobenzal-p-anisidine + p-anisal-p-phenetidine.

Fig. 2 - Mixed liquid crystal formation in the system p-ethoxybenzal-p-phenetidine + p-dimethylamine-benzal-p-phenetidine.

Fig. 3 - Mixed liquid crystal formation in the system p-ethoxybenzal-p-phenetidine + p-anisal-p-phenetidine.

Fig. 4 - Mixed liquid crystal formation in the system p-ethoxybenzal-p-phenetidine + p-nitrobenzal-p-phenetidine.

that p-anisal-p-phenetidine gives almost the same latent transition temperature 121.5 when studied separately with p-azoxyanisole[9] and p-acetoxybenzal-p-phenetidine. The latent transition point observed in this case is very near to its monotropic mesomorphic temperature[5-7].

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Influence of Molecular Structure on Liquid Crystalline Properties & Phase Transitions in Mixed Liquid Crystals in Smectic Phase

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A number of binary systems have been investigated with ethyl *p*-azoxybenzoate, a smectic liquid crystal as solvent and Schiff's bases as non-liquid crystalline solute. When the mesomorphic-isotropic temperatures of such binary systems are plotted against the mole per cent compositions of the liquid crystalline component, two types of transition curves, viz. (i) the usual curve where the transition line is depressed regularly and (ii) a rising curve exhibiting a maximum, are obtained. The latter type of curves indicates an enhancement in the smectic thermal stability, while the former type indicates a decrease in the smectic thermal stability, during the mixed liquid crystal formation.

MIXED liquid crystalline behaviour of binary mixtures in which one or both the components are nematic liquid crystals, has been reported earlier[1-6]. It was found that such mixtures possess a pronounced ability to form a homogeneous nematic melt over a certain range of temperature and concentration. More recently, Arnold and Sackmann[7] while studying the miscibility of liquid crystal phases have shown that two nematic phases of two different compounds are completely miscible and form a homogeneous nematic liquid crystalline region. Further, it was shown[7] that two smectic phases of two different compounds are likewise miscible forming a homogeneous smectic mesomorphic region. However, smectic phase of one compound and nematic phase of the other are not miscible.

Dave and Dewar[5] and later Dave and Lohar[6] in their studies on binary mixtures in which one component is a nematic liquid crystal and the other a non-liquid crystal have shown that the transition lines of binary systems in the phase diagrams provide a method for measuring the tendency of the non-mesomorphic component towards mixed mesomorphism; consequently, they obtained different values of group slopes for various end groups. The lower slope value indicates the greater tendency of non-mesomorphic component towards the mixed liquid crystal formation and vice versa. No such work seems to have been reported in binary mixtures where one component is a smectic liquid crystal and the other a non-mesomorphic one. Hence it was worth while to explore the possibility of mixed liquid crystal formation in smectic phase.

Materials and Methods

The precise measurements of various transition temperatures were made by using Leitz Ortholux polarizing microscope equipped with a heating arrangement.

Twenty-one systems of the above type have been studied, where ethyl *p*-azoxybenzoate (component A) — a prototype smectic liquid crystalline component — has been mixed with other non-mesomorphic Schiff's bases (component B, Table 1).

Analytical data of unknown compounds included in Table 1 are given in Table 2.

Results and Discussion

Compounds 1 to 20 (Table 1) are non-mesomorphic and do not exhibit liquid crystallinity either while heating or cooling and compound 21 is monotropic nematic. When solid-mesomorphic and mesomorphic-isotropic transition temperatures of these binary

TABLE 1 — NON-MESOMORPHIC SCHIFF'S BASES

Sl No	Component B	m.p. °C.
1	Methyl *p*-chlorobenzylidene-*p*-aminobenzoate	161·5
2	Methyl *p*-nitrobenzylidene-*p*-aminobenzoate	211·5
3	Ethyl *p*-nitrobenzylidene-*p*-aminobenzoate	180·0
4	*p*-Nitrobenzylidene-*p*-toluidine	124·0
5	*p*-Nitrobenzylidene-*p*-bromoaniline	163·0
6	*p*-Nitrobenzylidene-*p*-phenetidine	123·5
7	Methyl *p*-anisylidene-*p*-aminobenzoate	132·0
8	Methyl *p*-dimethylaminobenzylidene-*p*-aminobenzoate	163·5
9	*p*-Anisylidene-*p*-toluidine	93·0
10	*p*-Acetoxybenzylidene-*p*-bromoaniline	108·5
11	*p*-Chlorobenzylidene-*p*-phenetidine	123·0
12	*p*-Methylbenzylidene-*p*-toluidine	94·0
13	*p*-Dimethylaminobenzylidene-*p*-chloroaniline	152·0
14	*p*-Chlorobenzylidene-*p*-dimethylaminoaniline	164·0
15	*p*-Chlorobenzylidene-*p*-toluidine	128·0
16	Ethyl *p*-chlorobenzylidene-*p*-aminobenzoate	120·0
17	Ethyl *p*-anisylidene-*p*-aminobenzoate	80·0
18	*p*-Anisylidene-*p*-bromoaniline	120·0
19	*p*-Anisylidene-*p*-anisidine	148·0
20	*p*-Anisylidene-*p*-chloroaniline	92·0
21	*p*-Anisylidene-*p*-phenetidine*	128·5

*Transition temperature 122°C.

mixtures are plotted against the mole per cent of smectic compound, i.e. ethyl *p*-azoxybenzoate, two types of curves for smectic-isotropic transitions are obtained: (i) a usual curve where the transition lines are depressed regularly (Fig. 1), and (ii) a rising curve showing the maximum as observed in compounds 1 to 6 (Figs. 2 and 3). The maximum smectic-isotropic transition temperatures observed for compounds 1 to 6 are 127·0, 149·0, 139·5, 133·5, 138·0 and 147·5°C., respectively. In Table 3 are recorded solid to liquid or liquid crystal transformation temperatures of the binary systems, read from the phase diagrams and also the eutectic temperatures which are direct experimental values.

In Table 4 are recorded the smectic-isotropic transition temperatures of the binary systems. The values are obtained from phase diagrams.

A smectic mesophase is a system of stratified structure in which rod-shaped molecules lie parallel in each stratum. Another substance dissolved in such a liquid would be in an anisotropic environment and it would affect the properties of the mesomorphic substance in an unexpected manner. Unlike nematic mesophase, the smectic phase consists of strata of molecules and so some of the molecules of the compound dissolved in such a phase may occupy the place between smectic molecules in each stratum and the rest of the molecules may form a molecular stratum which may pack itself between the two strata of the smectic component, thus forming a homogeneous smectic melt. The tentative possible picture of such a melt is given in Fig. 4 (A and B) where *X* represents the molecules of ethyl *p*-azoxybenzoate and *Y* represents the molecules of

TABLE 2 — ANALYTICAL DATA OF UNKNOWN COMPOUNDS GIVEN IN TABLE 1

Sl No.	Nitrogen, %		Mol. formula
	Found	Reqd	
1	4·95	5·11	$C_{15}H_{12}ClNO_2$
2	10·29	9·86	$C_{15}H_{12}N_2O_4$
3	9·21	9·39	$C_{16}H_{14}N_2O_4$
7	5·29	5·20	$C_{16}H_{15}NO_3$
8	9·92	9·93	$C_{17}H_{18}N_2O_2$
13	11·26	10·83	$C_{15}H_{15}ClN_2$
16	4·62	4·86	$C_{16}H_{14}ClNO_2$
17	4·81	4·94	$C_{17}H_{17}NO_3$

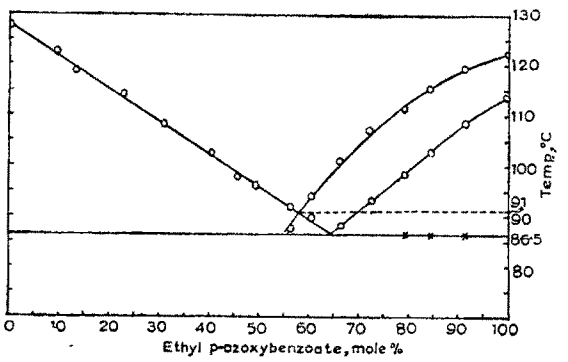

Fig. 1 — Plot of transition temperature against mole per cent of smectic compound for the system ethyl *p*-azoxybenzoate + *p*-chlorobenzylidene-*p*-toluidine

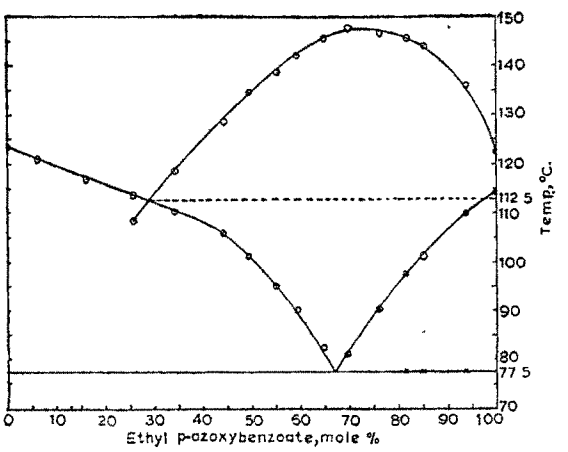

Fig. 2 — Plot of transition temperature against mole per cent of smectic compound for the system ethyl *p*-azoxybenzoate + *p*-nitrobenzylidene-*p*-phenetidine

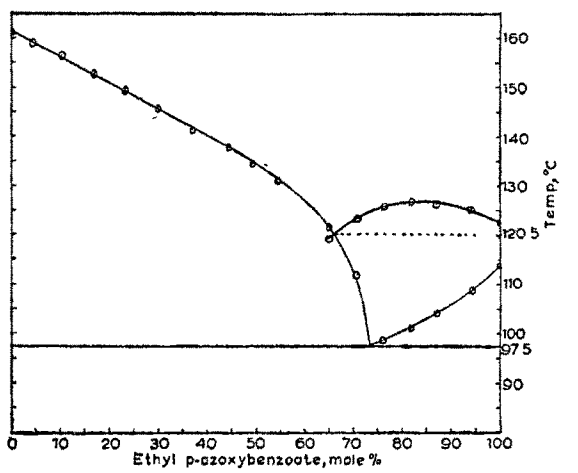

Fig. 3 — Plot of transition temperature against mole per cent of smectic compound for the system ethyl *p*-azoxybenzoate + methyl *p*-chlorobenzylidene-*p*-aminobenzoate

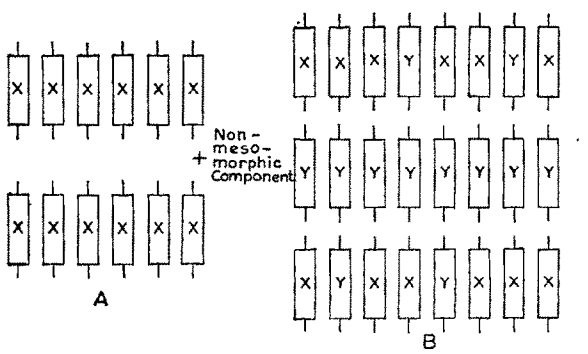

Fig. 4 — Structure of (A) smectic melt (pure) and (B) homogeneous smectic melt obtained as a result of dissolution of non-mesomorphic component

TABLE 3 — SOLID TO LIQUID OR LIQUID CRYSTAL TRANSITION TEMPERATURES FOR THE BINARY SYSTEMS

Non-mesomorphic compound*	Transition temperatures (°C.) at varying concentrations (mole %) of ethyl *p*-azoxybenzoate														Eutectic	
	0	10	20	30	40	50	60	70	75	80	85	90	95	100	Mole % of (A)	Temp
1	161·5	156·0	151·0	146·0	140·0	134·0	127·0	112·5	98·5	100·5	103·0	107·0	109·5	114·0	73·5	97·5
2	211·5	206·5	201·0	194·5	187·5	179·0	169·0	155·0	146·0	135·5	127·5	101·5	107·5	114·0	89·5	100·5
3	180·0	176·5	172·0	166·5	160·5	153·0	144·5	133·0	124·5	106·0	102·0	107·5	111·5	114·0	81·5	98·0
4	124·0	119·0	114·0	109·0	104·0	99·0	91·0	81·0	87·5	94·0	100·0	105·0	110·0	114·0	67·5	76·5
5	163·0	157·0	151·0	144·5	137·5	129·5	121·0	107·5	85·0	93·0	100 0	106·0	110·0	114·0	73·5	82·0
6	123·5	119·5	116·0	112·5	108·5	100·5	88·5	82·0	88·0	95·5	101·0	106·5	111·0	114·0	67·0	77·5
7	132·5	127·5	121·5	114·5	106·5	97·0	86·0	89·0	94·0	99·0	103·0	107·0	110·5	114·0	63·0	82·0
8	163·5	158·5	153·5	148·5	143·0	136·5	127·5	113·0	100·0	101·0	104·5	107·5	110·5	114·0	75·5	98·0
9	93·0	89·5	85·0	79·5	75·5	84·5	87·5	99·5	102·5	105·0	107·5	110·0	112·0	114·0	38·5	73·5
10	108·5	104·0	100·0	96·0	92·5	88·5	90·5	99·5	102·0	104·5	107·0	109·0	111·5	114·0	58·0	85·5
11	123·0	117·5	112·5	107·5	102·0	95·0	88·0	89·0	94·5	100·0	104·5	109·0	112·0	114·0	60·5	76·5
12	94·0	88·5	83·0	78·0	77·5	87·5	94·0	99·5	102·0	104·0	105·5	107·5	110 0	114·0	37·0	74·0
13	152·0	146·0	140·5	134·5	128·5	121·0	112·0	102·0	100·0	102·5	105·0	108·0	111·5	114·0	72 5	99·0
14	164·0	158·5	152·5	114·5	137·0	127·0	117·0	108·5	104·5	102·5	105·0	108·0	111·0	114·0	79 0	101·5
15	128·0	121·5	115·0	109·0	102·5	96·0	89·5	91·0	95·0	98·0	103·5	107·0	111·0	114·0	64·5	86 5
16	120·0	115·5	111·5	107·0	102·5	96·5	88·0	89·5	94·5	99·0	103·5	107·5	111·0	114·0	63·0	82·0
17	80·0	77·0	74·0	77·5	81·5	86·0	91·0	96·0	98·5	101·5	104·0	107·5	111·0	114·0	21·5	73·5
18	120·0	115·0	109·5	102·8	95·6	90·0	85·8	86·0	89·5	93·5	98·0	103·0	108·0	114·0	67 5	83·5
19	148·0	142·5	137·0	131·5	125·4	118·2	110·2	102·0	98·0	101·0	104·0	107·2	110·5	114·0	74·5	97·5
20	92·0	86·5	81·5	76·8	74·5	78·5	84·0	90·5	94·0	98·0	101·5	105·5	109·5	114·0	38·0	73·5
21	128·5	123·0	117·8	112·5	106·0	99·5	92·4	93·0	96·0	99·5	103 0	106·5	110·0	114·0	64·0	89 0

*Serial Nos refer to the compounds given in Table 1.

TABLE 4 — SMECTIC-ISOTROPIC TRANSITION TEMPERATURES FOR THE BINARY SYSTEMS

(Values in parentheses show monotropy)

Non-mesomorphic compound*	Transition temperatures† (°C.) at varying concentrations (mole %) of ethyl *p*-azoxybenzoate											Triple-point	
	30	40	50	60	70	75	80	85	90	95	100	Mole % of (A)	Temp.
1	—	—	—	—	123·0	125·5	126·5	127·0	126·5	125·0	122·5	66·0	120·5
2	—	—	—	—	(147·5)	148·5	148·5	147·0	143·0	137·5	122·5	73·5	148·5
3	—	—	—	(126·0)	—	138·0	139·5	139·0	136·5	132·0	122·5	70·0	133·0
4	—	—	111·0	123·0	130·0	132·0	133·0	133·5	132·0	129·5	122·5	45·5	101·5
5	—	—	—	(118·5)	129·5	134·0	137·0	137·5	136·5	132·0	122·5	61·0	119·5
6	114·0	125·0	134·5	143·0	147·0	147·0	146·0	143·5	139·5	133·0	122·5	29·0	112·5
7	—	—	98·5	105·0	110·5	113·0	115·0	117·0	119·0	121·0	122·5	49·0	98·0
8	—	—	—	(89·5)	100·0	104·5	109·0	113·0	116·5	119·5	122·5	74·0	103·5
9	—	—	—	—	—	—	(104·0)	110·0	115·5	119·5	122·5	81·5	106·0
10	—	—	—	—	—	(100·5)	109·0	114·0	117·5	120·0	122·5	75·5	102·0
11	—	—	108·5	114·0	118·0	119·5	121·0	122·0	122·0	122·5	122·5	40·0	102·0
12	—	—	—	—	—	—	(101·5)	106·5	112·0	117·5	122·5	84·0	105·5
13	—	—	—	(97·0)	105·0	108·5	111·5	114·5	117·5	120·0	122·5	68·5	104·0
14	—	—	—	—	111·0	113·5	115·5	117·5	119·5	121·0	122·5	68·0	110·0
15	—	—	—	93·0	104·0	108·5	112·5	116·0	118·5	121·0	122·5	58·0	91·0
16	—	—	99·0	107·5	113·5	116·0	117·5	119·5	120·5	121·5	122·5	49·0	97·5
17	—	(72·0)	(80·0)	(89·5)	(99·5)	104·0	108·5	112·5	116·0	119·5	122·5	62·0	91·5
18	—	—	(88·5)	98·0	106·0	109·0	112·5	115·0	118·0	120·2	122·5	50·8	89·5
19	—	—	—	—	(99·5)	102·5	105·8	109·5	103·5	118·0	122·5	71·5	100·5
20	—	(72·0)	85·5	96·5	106·0	109·8	113·2	116·2	119·0	121·0	122·5	41·5	74·8
21	—	—	—	(91·5)	101·0	105·0	108·6	112·5	116·0	119·0	122·5	60·5	92·0

*Serial Nos. refer to the compounds given in Table 1. †Binary systems containing 0, 10, 20 mole % of component A did not reveal transition temperatures.

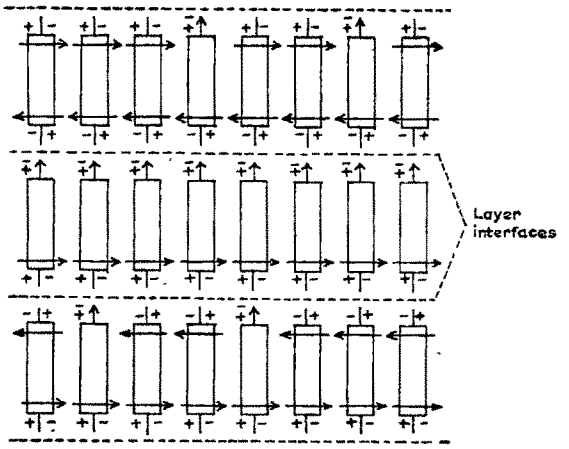

Fig. 5 — Arrangement of parallel molecules in layers wherein each molecule is perpendicular to layer interfaces

non-mesomorphic component. The degree of packing in this mode will depend upon molecular shape and size of the solute molecule and its functional groups. When the parallel molecules are arranged in layers where each molecule is perpendicular to the layer interfaces (Fig. 5) carrying terminal dipole moment parallel to major molecular axis as in *p*-substituted nitro- or chloro-compounds, it becomes logical to assume that the terminal dipoles due to such groups may disturb the efficiency of the dipoles of the other groups of neighbouring smectic molecules, causing reduction in lateral intermolecular attractions and quite naturally we may expect, reduced smectic thermal stability of the mixture, compared to pure smectic component. However, in the course of this study, some compositions of binary mixtures comprising a nitro-compound and in few cases a chloro-compound with ethyl *p*-azoxybenzoate, exhibit more smectic thermal stability than the pure smectic component, thus exhibiting a maximum when smectic-isotropic points are plotted against mole per cent of smectic component. It is rather difficult to explain such a behaviour. Gray and Byron[8] have explained the enhanced smectic thermal stability of 4-*p*-*n*-nonoxybenzylideneamino-4'-chlorobiphenyl in which C—Cl dipole acts parallel to the major molecular axis, by assuming that the molecules are tilted at an angle to the layer interfaces; by tilting the molecules away from the perpendicular arrangement, the separation of the positive and negative charges of C—Cl dipoles do not necessarily increase but positive charge of one dipole can be brought nearer to the negative centre of the neighbouring dipole. At some suitable angle, the attractive forces will outweigh the repulsive forces and the net energy of attraction will enhance the lateral attractions and the smectic properties.

In the mixtures studied here, the smectic component has two dipoles due to two terminal groups acting at an angle to the main molecular axis, while one dipole due to one of the two terminal groups of a non-mesomorphic component acts parallel and the other at an angle to the main molecular axis. If we consider the molecular arrangement of the mixture as shown in Figs. 4 and 5, to account for enhanced smectic properties of binary mixtures comprising non-mesomorphic compounds possessing terminal groups of high dipole moment (e.g. C—NO_2, etc.), the molecular strata formed in the smectic melt would be tilted at an angle to the planes of the smectic strata where the net energy of attraction can become effective to enhance the lateral attractions and the smectic properties.

Byron and Gray[8] have observed that in 4-*p*-*X*-benzylideneamino-4'-*n*-octoxybiphenyl when X represents —NO_2 or —Cl group, the nitro compound is thermally less stable than the corresponding chloro-compound. However, in the course of this study, when methyl *p*-chlorobenzylidene-*p*-aminobenzoate was mixed with ethyl *p*-azoxybenzoate, it gave a lower maximum of smectic-isotropic transition than the maximum obtained by mixing methyl *p*-nitrobenzylidene-*p*-aminobenzoate. From the limited data, it is difficult to explain the role of the terminally situated groups and their dipole moments on smectic characteristics of mixtures.

The study was carried out to deduce the slope of the transition curves in these binary mixtures similar to the study carried out by Dave and Dewar, and Dave and Lohar in nematic solutions. However, this is not possible as transition curves in these smectic mixtures are almost all curved and no order for the tendency of the polar groups present in the non-mesomorphic component, can be derived.

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