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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, 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*-dimethylaminobenzal-*p*-chloroaniline, m.p. 152° (Found: N, 11.36. Requires N, 10.85).

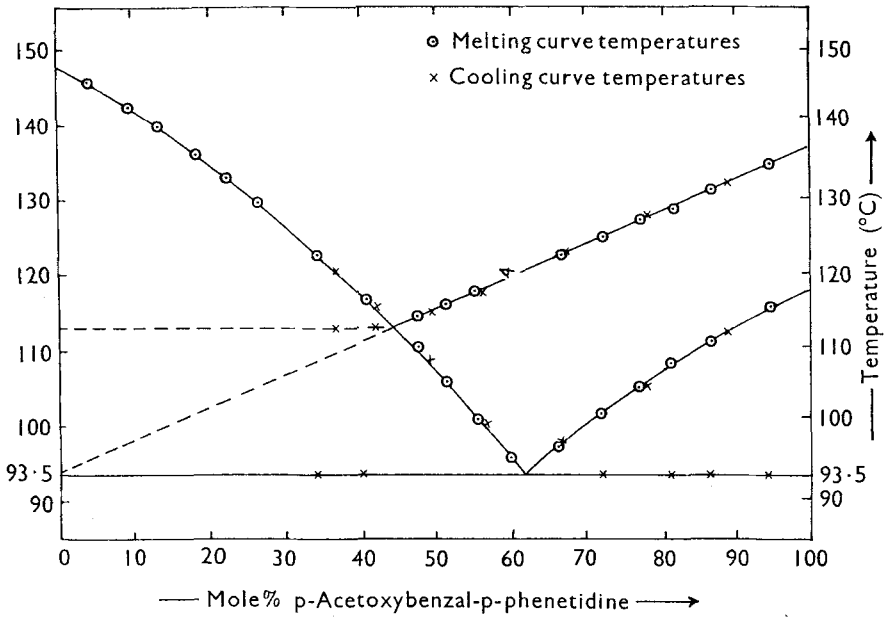
Method of Study

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.



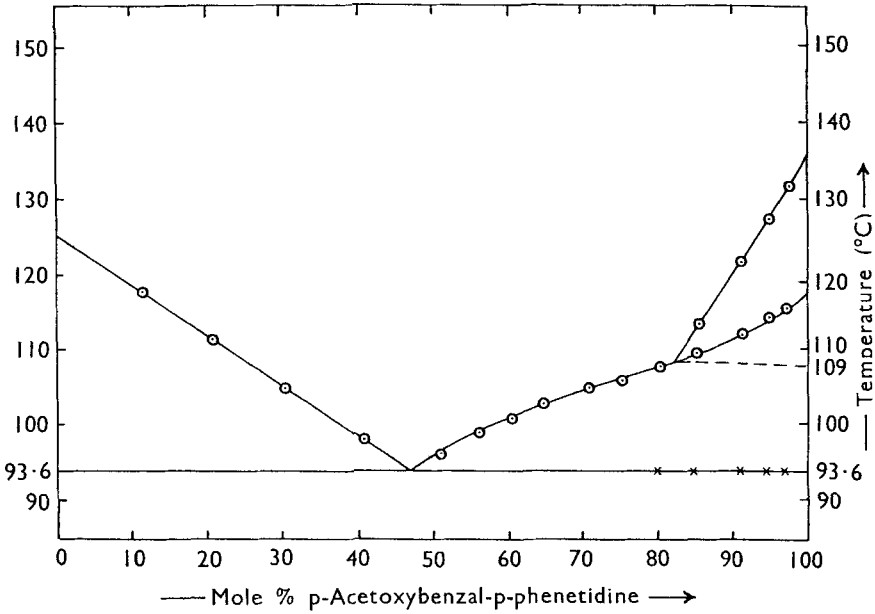
Phase diagram of

p-Acetoxybenzal-p-phenetidine:p-Anisal-p-anisidine

FIG. 1

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 simi-

larly 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



Phase diagram of
p-Acetoxybenzal-p-phenetidine:p-Chlorobenzal-p-bromoaniline

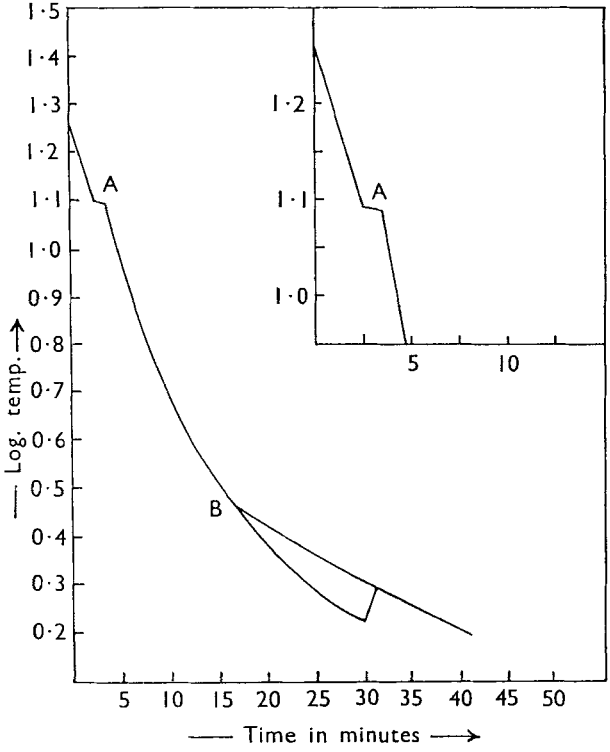
FIG. 2

are obtained and that the anisotropic liquid phase is a single homogeneous phase of mixed liquid crystals.

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

A—represents the liquid-liquid crystal transition.

B—the normal melting point.



A typical cooling curve of the system

p-Acetoxybenzal-p-phenetidine:p-Chlorobenzal-p-anisidine

(L.C) (N.L.C)

89·13 mole % L.C; Bath temp. = 104·3°C

FIG. 3

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.

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

TABLE 1 Transition Line Slopes for the Compounds of the Type $R \cdot C_6H_4 \cdot CH{=}N \cdot C_6H_4 \cdot R'$ with *p*-Acetoxybenzal-*p*-phenetidine (in °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
R= 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	2.0	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

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 $R \cdot C_6H_4 \cdot CH : N \cdot C_6H_4 \cdot R'$		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	120.0	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
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	93.0
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 $R \cdot C_6H_4 \cdot CH: N \cdot C_6H_4 \cdot R'$ R	R'	Mole % *p*-acetoxybenzal-*p*-phenetidine (Component A) 0	10	20	30	40	50	60	70	80	90	100	Triple point Mole % A	Triple point 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
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	108.0
13.	Cl	OCH_3	—	—	—	—	—	97.5	106.5	114.5	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

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 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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