D I S C U S S I O N

A : MIXED MESOMORPHISM IN THE NEMATIC PHASE

DISCUSSION

Liquid crystalline state is a state intermediate between a true crystal and a true liquid. This intermediate phase exhibits unique properties that are shared from both crystals and liquids. These crystalline and liquid properties exhibited by this phase are attributed to certain structural features of the molecules and also to the action of internal forces arising therefrom.

A nematic liquid crystal is a system which consists of long rod-shaped molecules, having more or less a translational freedom but only a restricted rotational freedom. It has a domain structure in which all the molecules in a given domain lie parallel to one another.

When any other substance is dissolved in such a nematic liquid, the dissolved substance will be in an anisotropic medium and its physical and chemical properties are affected in an interesting manner. Such mixtures yield mixed liquid crystals over a range of temperature and concentration. Binary mixtures of certain organic compounds which are non-liquid crystalline by themselves, also exhibit mixed liquid crystallinity over a suitable range of temperature and concentration. The binary systems studied in the present investigation exhibiting mixed liquid crystallinity are of two types : (1) the systems where one component is a mesomorphic substance, the other being a non-liquid crystal and (2) the systems where both the components are non-mesomorphic substances.

The binary systems of both these types studied during the course of this investigation are listed in Table 98.

Table 98

Binary systems of the type 1, where one component is a liquid crystal and the other is a non-liquid crystal.

I (a) Component A : p-Acetoxybenzal-p-phenetidine

(a liquid crystal)

mixed with

Component B : (a non-liquid crystal)

1. p-Anisal-p-anisidine.
2. p-Anisal-p-chloroaniline.
3. p-Anisal-p-bromoaniline.
4. p-Anisal-p-toluidine.
5. p-Anisal-p-iodoaniline.
6. p-Dimethylaminobenzal-p-phenetidine.
7. p-Nitrobenzal-p-chloroaniline.
8. p-Dimethylaminobenzal-p-fluoroaniline.
9. p-Chlorobenzal-p-toluidine.
10. p-Dimethylaminobenzal-p-chloroaniline.
11. p-Nitrobenzal-p-bromoaniline.
12. p-Chlorobenzal-p-phenetidine.
13. p-Ethoxybenzal-p-chloroaniline.
14. p-Dimethylaminobenzal-p-bromoaniline.
15. p-Anisal-p-phenetidine.
16. p-Dimethylaminobenzal-p-iodoaniline.

17. p-Nitrobenzal-p-iodoaniline.
18. p-Tolual-p-bromoaniline.
19. p-Chlorobenzal-p-bromoaniline.
20. p-Tolual-p-iodoaniline.
21. p-Chlorobenzal-p-iodoaniline.
22. p-Chlorobenzal-p-anisidine.
23. p-Diethylaminobenzal-p-diethylaminoaniline.
24. p-Chlorobenzal-p-diethylaminoaniline.
25. p-Anisal-p-diethylaminoaniline.
26. p-Dimethylaminobenzal-p-diethylaminoaniline.
27. p-Chlorobenzal-p-dimethylaminoaniline.
28. p-n-Propoxybenzal-p-anisidine.
29. p-n-Propoxybenzal-p-bromoaniline.
30. p-n-Propoxybenzal-p-dimethylaminoaniline.
31. p-n-Propoxybenzal-p-chloroaniline.
32. p-Chlorobenzal-p-nitroaniline.
33. p-Ethoxybenzal-p-phenetidine.
34. p-Tolual-p-toluidine.
35. p-Chlorobenzal-p-chloroaniline.
36. p-Nitrobenzal-p-phenetidine.
37. p-Nitrobenzal-p-anisidine.
38. p-Nitrobenzal-p-fluoroaniline.
39. p-Anisal-p-fluoroaniline.
40. p-Methoxybenzoic acid.
41. p-Ethoxybenzoic acid.
42. 4,4'-Dimethoxychalkone.
43. 4,4'-Dichlorochalkone.
44. 4,4'-Dichlorobenzalazine.

45. 4,4'-Di(dimethylamino)benzalazine.

I (b) Component A : p-Azoxyanisole (a liquid crystal)

mixed with

Component B : (a non-liquid crystal)

46. p-Anisal-p-iodoaniline.
47. p-Anisal-p-fluoroaniline.
48. p-Dimethylaminobenzal-p-fluoroaniline.
49. p-Nitrobenzal-p-fluoroaniline.
50. p-Nitrobenzal-p-bromoaniline.
51. 4,4'-Dimethoxy-3,3'-diacetylbiphenyl.
52. 6',6'''-Dihydroxy-4,4''-dimethoxy-3',3'''-bichalconyl.
53. 6',6'''-Dihydroxy-3',3'''-bichalconyl.
54. Triphenylmethane.
55. 2,2',6,6'-Tetramethoxybiphenyl.
56. 7-Benzoyloxy-3-benzoylflavone.

I (c) Component A : p-n-Butoxybenzoic acid (a liquid crystal)

mixed with

Component B : (a non-liquid crystal)

57. p-Nitrobenzal-p-phenetidine.
58. p-Anisal-p-anisidine.
59. p-Chlorobenzal-p-phenetidine.
60. p-Anisal-p-iodoaniline.
61. p-Nitrobenzal-p-iodoaniline.
62. p-Dimethylaminobenzal-p-phenetidine.
63. p-Nitrobenzal-p-chloroaniline.

64. p-Anisal-p-chloroaniline.

65. p-Nitrobenzoic acid.

66. p-Ethoxybenzoic acid.

67. p-Methoxybenzoic acid.

68. p-Chlorobenzoic acid.

69. p-Toluic acid.

70. p-Bromobenzoic acid.

71. p-Iodobenzoic acid.

72. p-Hydroxybenzoic acid.

I (d) Component A : p-n-Dodecyloxybenzal-p-n-butoxyaniline
(a smectic - nematic liquid crystal)
mixed with
Component B : (a non-liquid crystal)

73. p-Anisal-p-phenetidine.

74. p-Anisal-p-anisidine.

75. p-Dimethylaminobenzal-p-phenetidine.

76. p-Anisal-p-chloroaniline.

77. p-Anisal-p-bromoaniline.

78. p-Nitrobenzal-p-phenetidine.

79. p-Nitrobenzal-p-chloroaniline.

80. p-Nitrobenzal-p-bromoaniline.

II. Binary systems of the type 2, where both the components are non-liquid crystals by themselves.

81. p-Nitrobenzal-p-anisidine : p-Anisal-p-phenetidine.

82. p-Ethoxybenzal-p-phenetidine : p-Dimethylaminobenzal-p-phenetidine.

83. p-Ethoxybenzal-p-phenetidine : p-Anisal-p-phenetidine.

84. p-Ethoxybenzal-p-phenetidine : p-Nitrobenzal-p-phenetidine.

85. p-Nitrobenzal-p-anisidine : p-Nitrobenzal-p-phenetidine.

86. p-Nitrobenzal-p-anisidine : p-Anisal-p-anisidine.

87. p-Ethoxybenzal-p-phenetidine : p-Nitrobenzal-p-anisidine.

88. p-Ethoxybenzal-p-phenetidine : p-Nitrobenzal-p-nitroaniline.

89. p-Anisal-p-n-propoxyaniline : p-Anisal-p-n-butoxyaniline.

The term 'mesomorphism' has been referred to the phenomenon of liquid crystallinity and hence the term 'mixed mesomorphism' may be conveniently coined for the mixed liquid crystal phenomenon. However, both the terminologies will be frequently used throughout this discussion.

If the dissolved substance has the same molecular structure as that in which it is dissolved, the molecules of both solute and solvent will align themselves giving rise to a solution having a domain structure similar to that of the solvent. In other words, the two substances will form homogeneous mixed liquid crystals. If the solute molecules are of a different kind, they will be in an altogether different environment ; consequently they tend to bring about a disturbing effect on the orderly arrangement of the nematic liquid. The extent of such a disturbing effect will depend upon the structural difference of the solute and the solvent molecules. The random movement of the solute molecules will break up the regular parallel alignment of the molecules of the nematic liquid crystal and ultimately the nematic liquid tends towards the isotropic liquid. But till the concentration of the solute molecules increases to such an extent as to bring about complete disruption of the ordered structure of the solvent molecules, the mixture solution continues to exhibit mixed liquid crystallinity. This means that the extent of mixed liquid crystal formation will be different with different solute molecules in the same solvent.

It is a general concept that the addition of a substance to another substance lowers the melting point. In a mixture of two substances X and Y, the addition of X to component Y lowers the melting point of Y and vice versa. The depression in the melting point of a pure substance will be greater, the greater the amount of the second component added to it. For different compositions of a binary mixture, when these depressions are plotted, they form two curves called the melting point curves which meet in a point - the eutectic point - at which the two solids are in equilibrium with a liquid solution of definite composition corresponding with this point. In the present investigation one of the components of the binary mixtures is a mesomorphic substance having a melting point at which the substance melts to a crystalline turbid liquid and a higher transition temperature at which the turbid liquid becomes isotropic or clear. The addition of a non-liquid crystalline substance depresses both the melting and the transition points of the liquid crystalline substance. Now the depressions in such binary mixtures, on plotting give a third curve representing the depression in the transition points of the mixed melts in addition to the two usual melting point curves. The lowering effects thus caused on the two temperatures are,however, not the same and the two curves do not run parallel ; the effect on the transition temperature will depend upon the miscibility and the alignment of the solute molecules with those of the solvent. The transition curve, therefore, will meet the melting curve at some point and the region bounded by these curves will be the region of anisotropy. A reference to the graphs will reveal that the extent of this region of anisotropy differs with different solute molecules.

A number of binary systems consiting of p-acetoxybenzal-p-phenetidine, p-azoxyanisole or p-n-butoxybenzoic acid as the liquid crystalline component, the non-liquid crystalline component being either Schiff's bases or other suitable molecules, are studied. A general survey of the phase diagrams of these systems reveals that there are two notable effects which could be observed from the addition of the non-liquid crystalline solute molecules to the liquid crystalline substance. In the case of certain binary systems the region of anisotropy extends right across the eutectic point, the transition curve cutting the melting curve to the left of the eutectic, in which case the region of anisotropy will be bounded by the area BCDE (e.g., fig. 10) where B is the eutectic point. In several other binary systems, the transition curve intersects the melting curve to the right of the eutectic in which case the region of anisotropy will be bounded by the area CDE (e.g., fig.14). In the former the eutectic composition of the two components will be in equilibrium with the anisotropic liquid whereas in the latter, the eutectic composition of the two components will be in equilibrium with the isotropic liquid.

Thus, the binary systems may be classified under two categories - (i) where the transition curve cuts the melting curve to the left of the eutectic and (ii) where the transition curve cuts the melting curve to the right of the eutectic. However, the general effect in the nature of the depression of the transition points in both the cases is almost similar ; the transition curves seem to fall regularly along lines which may or may not be curved.

The behaviour of p-ethoxybenzoic acid and p-methoxybenzoic acid in mixture with p-acetoxybenzal-p-phenetidine, is different in that the transition curve first shows a depression and then cuts the melting curve to the left and the right of the eutectic point respectively. This indicates the possibility of a minimum in the transition curve. Dave and Dewar (140) and Lohar (160) observed a similar behaviour of p-methoxybenzoic acid and p-ethoxybenzoic acid separately in mixture with p-azoxyanisole. The mixtures of p-ethoxybenzoic acid and p-methoxybenzoic acid separately with p-n-butoxybenzoic acid, a liquid crystalline substance studied in the present investigation do not show any concavity in the transition curves but on the contrary, show a nearness to the linearity. In the binary systems like the above ones viz. p-acetoxybenzal-p-phenetidine with p-ethoxy-benzoic and p-methoxybenzoic acids wherein the components differ in structure, a concavity in the transition curve may be expected. When a substance different in structure is mixed with the liquid crystalline substance, generally there will be a difficulty in packing of the molecules together. The solute molecules will find difficulty in fitting in the domain structure of the solvent liquid crystalline molecules, and hence the capacity to resist the thermal agitation is lessened. The mesomorphic liquid phase undergoes transition to normal isotropic liquid at a temperature lower than that normally expected for isomorphous mixtures. In mixtures of substituted benzoic acids with the liquid crystalline p-n-butoxybenzoic acid there will be little or no difficulty in the packing of the molecules, the two components being isomorphous. The phase diagrams of these acid binary mixtures do not show any concavity and the transition lines are comparatively less steep which shows greater tendency towards mixed mesomorphism. Thus, in binary systems of dissimilar components, the transition curves show a possibility of a concavity which should increase to a rounded minimum with the increasing tendency of the non-liquid crystalline component towards mixed mesomorphism.

de Kock (22) has shown that the mixture of p-methoxycinnamic acid with p-azoxyanisole both of which are mesomorphic substances form a continuous series of liquid crystals and the transition curve exhibits a rounded minimum. This brings home the idea that if both p-methoxybenzoic acid and p-ethoxybenzoic acid were to form liquid crystals, then a minimum in the transition curves of these systems should be expected. The horizontal portion of the transition curves would then represent a part of the rounded minimum in a continuous series of mixed liquid crystals and normally these transition curves should have risen towards the side of p-methoxybenzoic acid and p-ethoxybenzoic acid respectively. Because of the presence of carboxylic group in p-methoxybenzoic and p-ethoxybenzoic acids, the two acids could be expected to be mesomorphic by dimerisation. Bennett and Brynmor Jones (100) have shown that these acids do not show mesomorphism individually due to their high melting points ; however, the mixture of these two non-liquid crystalline acids forms nematic mixed liquid crystals within a certain range of concentration, as a result of lowering in their melting points. Lohar (160) also studied this mixture and has reported mixed mesomorphism over a small range of temperature and concentration. Further, the para substituted alkoxybenzoic acids with groups OC_3H_7 and higher, exhibit mesomorphism individually. This supports the earlier view that the tendency towards concavity in the transition curves in binary systems of dissimilar components should increase to a rounded minimum with the increasing tendency of the end groups present in the non-mesomorphic components towards mixed mesomorphism.

Bogojawlensky and Winogradow (132) have shown that in a mixture of isomorphous substances the transition lines are almost linear. Walter (134) who studied the mixture of anisic acid and p-methoxycinnamic acid has reported about the linearity of the transition line. Prins (139) has shown that in the case of the mixture of p-azoxyanisole and p-azoxyphenetole the transition line is linear whereas in the case of the mixture of p-azoxyphenetole and p-methoxycinnamic acid it is rounded with a minimum. In the present investigation the mixtures of p-acetoxybenzal-p-phenetidine separately with p-methoxybenzoic acid and p-ethoxybenzoic acid show a concavity in the transition lines whereas in the mixtures of p-acetoxybenzal-p-phenetidine and non-mesomorphic Schiff's bases, the transition lines are almost linear. This shows that the transition lines would be linear if the molecules are similar and would deviate from linearity when the molecules of the two components are dissimilar.

Diverse views have been expressed about the composition of this anisotropic liquid. This initiated the investigation to examine whether this anisotropic liquid is a one-phase region of a homogeneous solution or a two-phase region.

The phase diagrams drawn on the basis of the observations by optical method give no specific indication of two phases coexisting in the anisotropic region. But this cannot be taken as a definite evidence as it is difficult to observe the phase change through heating and therefore, some of the systems were examined by the thermal cooling method applying very low rates of cooling as the heat of transition from isotropic to anisotropic is very low. The absence of invariant lines in the diagrams clearly suggests that there are no two-phase liquid regions. An examination of a typical cooling curve (fig.7) shows that at the transition point of isotropic liquid to anisotropic liquid there is an extremely small break in the cooling curve which only extends over a very small range of temperature - at the most, one degree. This range remains almost constant with mixtures of different compositions of the same two components. If there

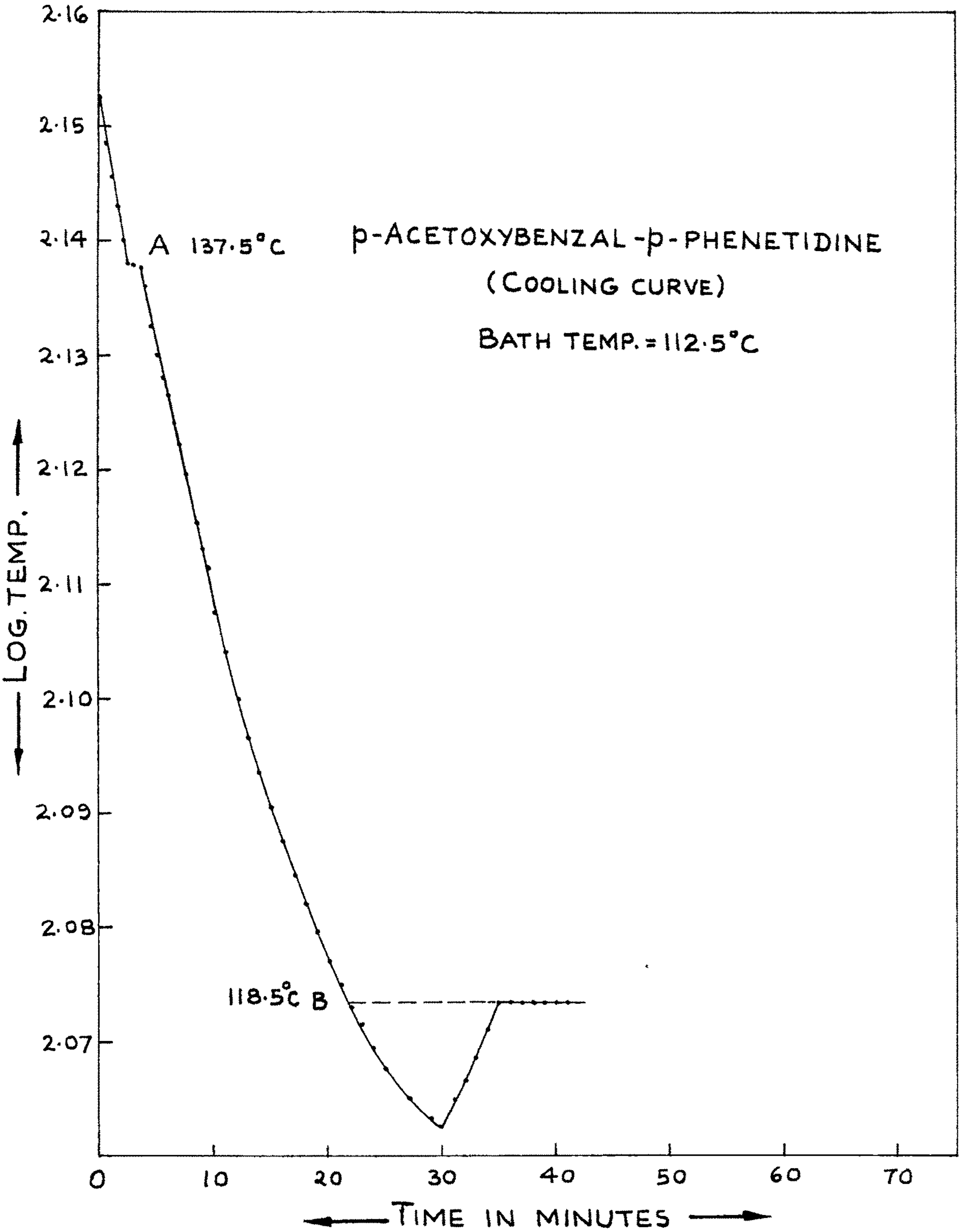

p-ACETOXYBENZAL-p-PHENETIDINE
(COOLING CURVE)
BATH TEMP. = 112·5°C
A 137·5°C
118·5°C B
LOG. TEMP.
2·16
2·15
2·14
2·13
2·12
2·11
2·10
2·09
2·08
2·07
0
10
20
30
40
50
60
70
TIME IN MINUTES

FIG. 99

existed a two-phase region, then the range of this break in the cooling curve at the isotropic - anisotropic transition would not be uniform with different compositions of the same two components. Further, this isotropic-anisotropic transition break is similar to the corresponding break observed in the cooling curve for pure p-acetoxybenzal-p-phenetidine, the liquid crystalline component (fig. 99). A detailed examination of the phase diagrams should provide valuable information.

The phase diagrams have been already classified into two categories : (i) in which the eutectic mixture is in equilibrium with the anisotropic liquid and (ii) in which the eutectic mixture is in equilibrium with the isotropic liquid. In both the types of phase diagrams, the transition curve cuts the melting curve in point E ; in type (i) it cuts to the left of the eutectic, while in type (ii) it cuts to the right of the eutectic. Generally in a binary system the melting curve represents an equilibrium between the solid component and the isotropic liquid solution. In the phase diagrams of the binary systems studied here, it can be seen that part of the melting curve represents an equilibrium between the solid and the anisotropic liquid and this anisotropic liquid in turn is in equilibrium with the isotropic liquid through the transition curve. These two curves meet in point E and at this point all the three phases - solid, isotropic liquid and anisotropic liquid will be in equilibrium ; the temperature of this point shown by the broken line in the diagrams will be the temperature at which the phase change from anisotropic to isotropic and vice versa will take place. This point at which all the three phases coexist may be called the invariant transition point. In the diagrams of the type (i) the broken line EF is to the left of the eutectic, whereas in the diagrams of the type (ii) it is to the right of the eutectic. According to the phase rule in any diagram of the type (i), any composition to the right of the invariant point when heated above the eutectic temperature, will first change into solid + anisotropic liquid, which on further heating will dissolve into anisotropic solution along the melting curve and then change into isotropic liquid along the transition curve, whereas the compositions to the left of the invariant point when heated above the eutectic temperature will first change into solid + anisotropic liquid, but this when further heated, on obtaining the temperature corresponding to the invariant point E, the anisotropic liquid will change into isotropic liquid and above the broken line EF there will be solid + isotropic liquid which on further heating will dissolve into isotropic liquid along the melting curve.

Thus, when an isotropic solution of a composition to the left of the point E and above the melting curve is cooled, the cooling curve will first show a break usually accompanied by supercooling at the melting curve, and on further cooling, the cooling curve again shows a small break at the broken line EF corresponding to the temperature of the point E ; this break is of the same type and almost the same magnitude as the break observed along the transition curve for change from isotropic to anisotropic liquid. A study of the systems p-acetoxybenzal-p-phenetidine : p-anisal-p-anisidine ; p-acetoxybenzal-p-phenetidine : p-nitro-benzal-p-chloroaniline and p-acetoxybenzal-p-phenetidine : p-chlorobenzal-p-anisidine (figs. 10,16,31) will reveal that different compositions of a mixture show breaks at the same temperature along the broken line EF and these breaks are of the same type and magnitude as the transition curve breaks. This indicates that for the compositions to the left of the point E, the anisotropic liquid changes to isotropic liquid at the temperature of the point E along the broken line EF. This is further supported by the fact that if any solid mixture of a composition to the left of the point E, is heated in a small capillary tube to a temperature below the temperature of the broken line and above the eutectic temperature, and is allowed to stand for some time at the same temperature, the mixture separates into solid particles settling down and the anisotropic liquid. On the contrary, the same mixture at the temperature between the broken line and the melting curve, separates into solid particles and the isotropic liquid.

In the case of the diagrams of the type (ii), all the compositions on either side of the eutectic, on heating above the eutectic temperature will first change into solid + isotropic liquid, which on further heating will dissolve into isotropic liquid solution along the melting curve except the compositions to the right of the point E.

Mixtures of any composition to the right of the point E, above the temperature corresponding to the eutectic point will first change into solid + isotropic liquid and this liquid at the temperature of the point E will change into anisotropic liquid and above the line EF there will be solid + anisotropic liquid. This solid + anisotropic liquid, on further heating will dissolve into anisotropic liquid along the melting curve and will finally change to isotropic liquid along the transition curve.

If an isotropic solution of any composition to the right of the point E and above the transition line is cooled, the cooling curve first shows a small break at the transition line as usual and then it shows another break usually accompanied by supercooling at the melting curve. On further cooling, a break in the curve should be expected at the broken line corresponding to the temperature of point E as in the diagrams of type (i). However, it could not be definitely observed. This is probably due to the fact that in type (i) the change takes place from isotropic to anisotropic with the liberation of heat whereas in the case of type (ii) the change is in the reverse order and hence probably no significant break could be observed.

This break in the cooling curves in the phase diagrams is consistent in magnitude and type and is similar to that observed in the case of a pure nematic liquid crystal, p-acetoxybenzal-p-phenetidine. This indicates that the change from isotropic to anisotropic and vice versa takes place through the invariant transition point E. If at all there existed an invariant line at the point E indicative of a two-phase region, the magnitude of the break along the broken line EF should decrease as one proceeds away from the point E ; but this is not so observed. Further, there appears no other break in the cooling curve throughout the anisotropic region.

de Kock (22) and Prins (139) who studied binary mixtures of substances one or both of which may be liquid crystalline, have suggested that there should be a range of temperature over which the two liquid phases-isotropic and anisotropic could coexist. Dave and Dewar (140) repeated one of the binary systems viz. mixture of p-azoxyanisole and quinol, studied by Kock, applying very low rates of cooling and carefully observing the breaks. Their observations agree well with those obtained in the present investigation. The magnitudes of the breaks at the isotropic-anisotropic transition were all the same for mixtures of different compositions, and they found no other break in the anisotropic region. Based on the principles of thermodynamics they concluded that either the two-phase region did not exist at all or if it did exist, it is only in a very small, almost negligible area ; but in any case the region of coexistence of two liquid phases was not of that magnitude as suggested by Kock.

This indicates that the anisotropic region is a single phase region of a homogeneous solution exhibiting birefringence.

This conclusion is further supported by observing the transitions when the mixtures are examined on the Leitz Ortholux polarizing microscope fitted with a heating stage. When the mixture on the slide, exhibiting anisotropy is heated to isotropic liquid and allowed to cool slowly, the transition from isotropic liquid to mesomorphic state could be marked clearly by the appearance of nematic bubbles at a stretch. 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 state 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.

Another interesting aspect of this homogeneous anisotropic liquid is the degree of disturbance caused on it by the solute molecules. Depending on the dissimilarities of the solvent and solute molecules, the specific parallel orientation of the molecules in a nematic mesomorphic melt will be disturbed to a more or less extent. If the solute molecules are structurally compatible with the mesomorphic molecular arrangement, they should be expected to get adjusted to the parallel alignment of the nematic liquid, and mixed liquid crystals may be expected to form over a wider area in the phase diagrams. Most favourable conditions for mixed liquid crystal formation would arise if the solute molecules are long and lath-shaped. As the structural similarities of the solute and the solvent molecules depart more and more, the extent of disturbance should be greater and greater, and theoretically at least, there should arise a condition when the effect of disturbance by the non-liquid crystalline dissimilar solute molecules would be maximum so as to cause a total destruction of the liquid crystalline properties of the mesomorphic substance. Gray (102) has also mentioned that if the non-mesomorphic component consisted of bulky spherical molecules, then the parallel distribution of the molecules of the mesomorphic system would be difficult to maintain ; the mesomorphic-isotropic transition temperature would probably be depressed more than the melting point, and no liquid crystalline properties would be observed.

In the present investigation, p-azoxyanisole is studied separately with some non-mesomorphic odd molecules and the extent of the mixed liquid crystal formation of these mixtures is given in Table 99.

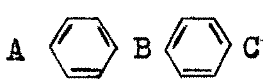
Table 99

No.	Odd molecules	Mole % of non-liquid crystal component
1.	4,4'-Dimethoxy-3,3'-diacetyl - biphenyl.	5.8
2.	6',6'''-Dihydroxy-4,4''-dimethoxy-3',3'''-bichalconyl.	4.8
3.	6',6'''-Dihydroxy-3',3'''-bichalconyl.	4.5
4.	Triphenylmethane.	4.8
5.	2,2',6,6'-Tetramethoxybiphenyl.	4.5
6.	7-Benzoyloxy-3-benzoylflavone.	4.5

In the case of the mixture of p-azoxyanisole with 7-benzoyloxy-3-benzoylflavone, mixed liquid crystals are formed only up to 4.5 mole per cent of flavone. Further addition of flavone completely disturbs the parallel orientation of the solvent molecules and the mixture shows no liquid crystallinity. The molecules of flavone differing widely in structure compared to the solvent molecules,find it difficult to adjust to the parallel orientation of the solvent molecules beyond a certain concentration. The internal molecular forces which are responsible for the parallel orientation of the nematic liquid are ruptured by somewhat bulky molecules of flavone ; however, the disturbing effect is limited up to a certain minimum as it can be seen from the phase diagram (fig. 65) that the mixed mesomorphism is exhibited up to 4.5 mole per cent additions of flavone. Similarly, 4,4'-dimethoxy-3,3'-diacetylbiphenyl, 6',6'''-dihydroxy-4,4''-dimethoxy-3',3'''-bichalconyl, 6',6'''-dihydroxy-3',3'''-bichalconyl, triphenylmethane and 2,2',6,6'-tetramethoxybiphenyl are dissimilar in shape and structure compared to p-azoxyanisole and the phase diagrams of these substances individually with p-azoxyanisole show that genuine mixed liquid crystals are formed up to about 4.5 mole per cent of the non-liquid crystalline component.

It can therefore be said that irrespective of the dissimilarity in structure, difference in shape and size of the solute molecules, there always exists a certain minimum area over which genuine mixed liquid crystals are formed. The extent of mixed mesomorphism varies with the non-liquid crystalline component and gradual increase in the area can be expected as the solute molecules approach the solvent molecules in shape, size and structure.

During this investigation, a number of binary systems comprising p-acetoxybenzal-p-phenetidine as the liquid crystalline component and Schiff's bases possessing various terminal groups as the non-liquid crystalline component, have been examined. Here, both the components are aromatic compounds of the type

 where A and C are the terminal

groups and B a mildly polar CH = N group. The two components being structurally similar, the long rod-shaped non-liquid crystal component will readily align in the anisotropic environment and the slope of the transition line will be a measure of the miscibility of the two molecules and hence the extent of mixed liquid crystal formation. The greater the dissimilarity of the two molecules, the steeper will be the slope of the liquid -liquid transition lines. This might be expected; for, the disturbing effects of the solute on the mesomorphic phase should be greater, the smaller the tendency of the solute molecules themselves to give oriented melts. It can be observed from the phase diagrams that the slopes of the transition lines in the binary systems vary with the change of the end groups in the non-liquid crystalline molecules. The non-liquid crystalline Schiff's bases selected for the study possess different terminal groups, like $-NO_2$, $-OC_2H_5$, $-OCH_3$, $-OC_3H_7$, $-N(CH_3)_2$, -Cl, $-CH_3$, -Br, -I, -F and $-N(C_2H_5)_2$; some of these are sufficiently polar, others being mildly polar. The measured initial slopes of the mesomorphic-isotropic transition lines for the various binary systems comprising p-acetoxybenzal-p-phenetidine as a liquid crystal are listed in Table 100. The binary systems marked with an asterisk are also studied with p-azoxyanisole and the same slope values are obtained.

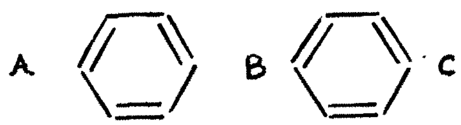
The variation in the slopes of the transition lines should be expected because the polar groups at the

Table 100

p-Acetoxybenzal-p-phenetidine (liquid crystal)

Mixed with

Non-liquid crystalline compound of the type :



No.	A	B	C	Slope of the transition line. (^{o}C / mole %) x 10
1.	OCH_3	CH:N	OCH_3	4.0
2.	OCH_3	CH:N	Cl	9.0
3.	OCH_3	CH:N	Br	10.0
4.	OCH_3	CH:N	CH_3	9.0
5.	*OCH_3	CH:N	I	13.0
6.	$(CH_3)_2N$	CH:N	OC_2H_5	6.5
7.	NO_2	CH:N	Cl	7.8
8.	*$(CH_3)_2N$	CH:N	F	14.0
9.	Cl	CH:N	CH_3	14.5
10.	$(CH_3)_2N$	CH:N	Cl	12.8
11.	*NO_2	CH:N	Br	9.0
12.	Cl	CH:N	OC_2H_5	8.3
13.	OC_2H_5	CH:N	Cl	8.3
14.	$(CH_3)_2N$	CH:N	Br	14.1
15.	OCH_3	CH:N	OC_2H_5	3.0
16.	$(CH_3)_2N$	CH:N	I	16.5
17.	NO_2	CH:N	I	11.5
18.	CH_3	CH:N	Br	15.75
19.	Cl	CH:N	Br	15.75

Table 100 (Contd.)

20.	CH_3	CH:N	I	18.1
21.	Cl	CH:N	I	18.1
22.	Cl	CH:N	OCH_3	9.0
23.	$(C_2H_5)_2N$	CH:N	$(C_2H_5)_2N$	34.5
24.	Cl	CH:N	$(C_2H_5)_2N$	24.5
25.	OCH_3	CH:N	$(C_2H_5)_2N$	19.2
26.	$(CH_3)_2N$	CH:N	$(C_2H_5)_2N$	22.7
27.	Cl	CH:N	$(CH_3)_2N$	12.8
28.	OC_3H_7	CH:N	OCH_3	4.5
29.	OC_3H_7	CH:N	Br	11.0
30.	OC_3H_7	CH:N	$(CH_3)_2N$	8.0
31.	OC_3H_7	CH:N	Cl	9.5
32.	Cl	CH:N	NO_2	7.5
33.	OC_2H_5	CH:N	OC_2H_5	2.0
34.	CH_3	CH:N	CH_3	14.4
35.	Cl	CH:N	Cl	14.4
36.	NO_2	CH:N	OC_2H_5	1.5
37.	NO_2	CH:N	OCH_3	2.4
38.	* NO_2	CH:N	F	9.0
39.	* OCH_3	CH:N	F	10.4
40.	OCH_3	COOH COOH	OCH_3	Concavity
41.	OC_2H_5	COOH COOH	OC_2H_5	Concavity
42.	OCH_3	CO.CH:CH	OCH_3	16.0
43.	Cl	CO.CH:CH	Cl	18.5
44.	Cl	CH:N.N:CH	Cl	5.5
45.	$(CH_3)_2N$	CH:N.N:CH	$(CH_3)_2N$	6.6

ends of the molecules help to increase the intermolecular adhesions which in turn help in maintaining the parallel alignment of the nematic melt, in addition to increasing the length of the linear molecule. On the other hand, the absence of polar end groups will weaken the intermolecular adhesions, thus slowly breaking the parallel orientation in the nematic melt.

Thus, it should be possible to find out the tendency of the non-mesomorphic component towards mixed mesomorphism in terms of the efficiency of the various groups present in it. From the slopes of the transition lines, the relative effect of different groups can be obtained. This can be done by considering the effects due to different compounds of the same series having a common group at one end and different groups at the other. Davė and Dewar (141) in their study of mixed liquid crystals with p-azoxyanisole, found that the difference between the Schiff's base compounds having either methyl or methoxy group at one end and different common groups at the other end remains almost the same, about 5.0. A few such pairs of Schiff's bases which should belong to the series of compounds considered by them for such a purpose, are studied in this investigation with another liquid crystal, p-acetoxybenzal-p-phenetidine, a Schiff's base compound, and the difference in the slopes of the transition lines for these pairs is given in the following Table 101.

Table 101

	Cl	Br	I
OCH_3	9.0	10.0	13.0
CH_3	14.4	15.75	18.1
Difference	5.4	5.75	5.1

The difference value obtained here compares fairly well with the value obtained by Dave and Dewar (141) in their study of mixed liquid crystals with p-azoxyanisole as the liquid crystalline component.

With a view to find out the relative effects of different groups towards mixed mesomorphism, Lohar (160) examined different such pairs of Schiff's base compounds in mixture with p-azoxyanisole and observed that the difference values in the slopes of the transition lines for different pairs of Schiff's base series with common groups at one end and fixed different groups at the other are almost the same. Several such pairs of Schiff's base series as examined by Lohar are studied in the present investigation in mixture with p-acetoxybenzal-p-phenetidine, a liquid crystalline Schiff's base. The difference values obtained in the slopes of the transition lines for such series are given in Table 102.

The difference,in nitro and dimethylamino series is 5.0, in methoxy and ethoxy series is round

Table 102

	OC_2H_5	Cl	F	Br	I
$(CH_3)_2N$	6.5	12.8	14.0	14.1	16.5
NO_2	1.5	7.8	9.0	9.0	11.5
Difference	5.0	5.0	5.0	5.1	5.0

	Cl	$(CH_3)_2N$
OCH_3	9.0	7.5*
OC_2H_5	8.3	6.5
Difference	0.7	1.0

	OCH_3	Br	I	$(CH_3)_2N$
CH_3	9.0	15.75	18.1	12.7*
Cl	9.0	15.75	18.1	12.8
Difference	0.0	0.0	0.0	0.1

about 1.0, which becomes zero or a negligible value of 0.1 in methyl and chloro series. These values compare well with those obtained by Lohar (160). The fact that the difference in the slopes of the transition lines of substances in pairs of Schiff's base series where the non-liquid crystalline Schiff's bases have different common groups at one end and fixed different groups at the other can be zero, evolves an interesting point. The effects of methyl and chloro groups are shown to be equal (141,160).

Some more such pairs of series are examined with p-acetoxybenzal-p-phenetidine and are tabulated in Table 103.

Table 103

	OCH_3	Cl	$(CH_3)_2N$
OC_3H_7	4.5	9.5	8.0
OCH_3	4.0	9.0	7.5*
Difference	0.5	0.5	0.5

	OCH_3	Cl	$(CH_3)_2N$
OC_3H_7	4.5	9.5	8.0
OC_2H_5	3.0	8.3	6.5
Difference	1.5	1.2	1.5

	Cl	F	Br	I	$(C_2H_5)_2N$
$(CH_3)_2N$	12.8	14.0	14.1	16.5	22.7
OCH_3	9.0	10.4	10.0	13.0	19.2
Difference	3.8	3.6	4.1	3.5	3.5

	OCH_3	Cl	Br	I
CH_3	9.0	14.5	15.75	18.1
NO_2	2.4	7.8	9.0	11.5
Difference	6.6	6.7	6.75	6.6

Table 103 (Contd.)

	OC_2H_5	Cl	Br	I
Cl	8.3	14.4	15.75	18.1
NO_2	1.5	7.8	9.0	11.5
Difference	6.8	6.6	6.75	6.6

	NO_2	OCH_3	$(CH_3)_2N$	Cl
Br	9.0	10.0	14.1	15.75
OC_2H_5	1.5	3.0	6.5	8.3
Difference	7.5	7.0	7.6	7.45

	OCH_3	Cl
$(C_2H_5)_2N$	19.2	24.5
$(CH_3)_2N$	7.5 *	12.8
Difference	11.7	11.7

	OCH_3	$(CH_3)_2N$
$(C_2H_5)_2N$	19.2	22.7
OC_3H_7	4.5	8.0
Difference	14.7	14.7

Table 103 (Contd.)

	$(CH_3)_2N$	Cl
$(C_2H_5)_2N$	22.7	24.5
OCH_3	7.5 *	9.0
Difference	15.2	15.5

	OCH_3	$(CH_3)_2N$	Cl
$(C_2H_5)_2N$	19.2	22.7	24.5
OC_2H_5	3.0	6.5	8.3
Difference	16.2	16.2	16.2

The slope of the transition lines marked with an asterisk in Tables 102 and 103 are taken from the binary systems studied by Lohar (160) with p-azoxy-anisole as a liquid crystal.

In table 104 are given some solitary pairs of Schiff's bases with a common group at one end and different groups at the other.

Table 104

	Cl		Cl		Cl
$(C_2H_5)_2N$	24.5	I	18.1	Br	15.75
NO_2	7.8	NO_2	7.8	NO_2	7.8
Difference	16.7		10.3		7.95

The difference values in these cases are high and should indicate the approximate difference values for such relevent series of Schiff's bases if and when studied.

It can be seen that the difference in the slopes of the transition lines in pairs of Schiff's base series with common groups at one end and fixed different groups at the other in all these systems is almost the same which shows that the effects of the terminal groups are specific and approximately additive.

On the basis of the above discussion, the effect of different terminal groups can be deduced in terms of 'group slopes'. Consider the binary system p-acetoxybenzal-p-phenetidine : p-anisal-p-anisidine (fig.10), the transition line of which has a slope value equal to 4.0. In this case the admixed non-liquid crystalline Schiff's base has an OCH_3 group at either end. As the effect of terminal groups is additive, the group slope value for each OCH_3 group will be 2.0. Knowing the value of a certain group, the values for the other groups can be similarly calculated, bearing in mind that the effects of groups are additive. For example, the slope of the transition line of the binary system p-acetoxybenzal-p-phenetidine : p-anisal-p-iodoaniline is 13.0 (Table 100). The non-liquid crystalline component has OCH_3 and I as terminal groups. The value of group slope for OCH_3 is 2.0 and hence the group slope value for the iodo group will be 11.0.

In this way group slope values for various terminal groups can be deduced. From the slopes of the transition lines of binary systems of p-azoxyanisole and Schiff's bases Dave and Dewar (141) and later Dave and Lohar(142) deduced values of group slopes for many terminal groups. A comparison of these with the group slope values deduced for the corresponding groups from the binary systems of p-acetoxybenzal-p-phenetidine, a liquid crystalline Schiff's base and other non-liquid crystalline Schiff's bases studied in the present investigation, is given in Table 105. The values of the present investigation compare well with those obtained by them with p-azoxy-anisole, a liquid crystalline substance.

Table 105

End groups	NO_2	OC_2H_5	OCH_3	$N(CH_3)_2$	Cl	CH_3	Br	I
Group slope values in the present work with p-acetoxy-benzal-p-phenetidine as liquid crystal.	0.5	1.0	2.0	5.6	7.2	7.2	8.5	11.0
Group slope values by previous workers with p-azoxyanisole as liquid crystal.	0.5	1.0	2.0	5.6	7.2	7.2	8.9	12.5

Many other Schiff's bases having end groups OC_3H_7, F, $N(C_2H_5)_2$ are studied in mixture with p-acetoxybenzal-p-phenetidine as the liquid crystalline component ; some of these are also studied with p-azoxyanisole. The relative group slope values are given in Table 106.

Table 106

End groups	I	F	OC_3H_7	$N(C_2H_5)_2$
Group slopes with p-acetoxybenzal-p-phenetidine.	11.0	8.4	2.5	17.2
Group slopes with p-azoxyanisole.	11.0	8.4	-	-

It can be seen that the group slope values remain the same whether the liquid crystalline component is p-acetoxybenzal-p-phenetidine or p-azoxyanisole.

Based on the magnitudes of these group slope values, an order of group efficiency for mixed liquid crystal formation can be derived. Dave and Dewar (141) and Lohar (160) obtained such an order in their study of binary systems comprising p-azoxyanisole as a liquid crystal. The two orders for the corresponding groups are compared below in Table 107.

Table 107

Oder of group efficiency in the descending sequence.

NO_2 >	OC_2H_5 >	OCH_3 >	$N(CH_3)_2$ >	Cl =	CH_3 >	Br >	I
0.5	1.0	2.0	5.6	7.2	7.2	8.5	11.0

(Present investigation with p-acetoxybenzal-p-phenetidine as a liquid crystal component)

NO_2 >	OC_2H_5 >	OCH_3 >	$N(CH_3)_2$ >	Cl =	CH_3 >	Br >	I
0.5	1.0	2.0	5.6	7.2	7.2	8.9	12.5

(Previous workers with p-azoxyanisole as a liquid crystal component)

The results in Table 107 indicate that the two orders compare very well. It can be seen that irrespective of the liquid crystalline component, the efficiency of the end groups operate in the same order provided the two components are isomorphous. On the basis of some more end groups studied in this investigation the extended order of efficiency will be as under :

Table 108

NO_2 >	OC_2H_5 >	OCH_3 >	OC_3H_7 >	$N(CH_3)_2$ >	CH_3 =	
0.5	1.0	2.0	2.5	5.6	7.2	
Cl >	F ≥	Br >	I >	$N(C_2H_5)_2$		
7.2	8.4	8.5	11.0	17.2		

Dave and Dewar (141) and later Lohar (160) have reported that CH_3 and Cl groups have the same effect, although their polarities differ. The results of the present investigation given below reveal that

	(^{o}C / mole %) x 10
$Cl.C_6H_4.CH{:}N.C_6H_4.CH_3$	14.5
$Cl.C_6H_4.CH{:}N.C_6H_4.Cl$	14.4
$CH_3.C_6H_4.CH{:}N.C_6H_4.CH_3$	14.4

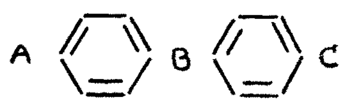
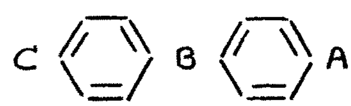
the value of the slopes of the curve is about 14.4 whether there are two CH_3 groups, two Cl groups or one CH_3 and one Cl group at the ends of the molecule. This has been attributed to the similar size of CH_3 and Cl groups (141,160). Gray (102) also mentions that the nematic - isotropic temperatures of isomeric methyl and chloro substituted compounds are always closely similar. The size and shape of the terminal groups may, therefore, be important factors.

In these binary systems both the mesomorphic and non-mesomorphic components being Schiff's bases, the structural modes remain the same throughout, the only variable factor being the polar end groups. The change in the slopes of the transition lines, should, therefore, be simply related to these end groups. The order of efficiency deduced from the slopes of the transition lines, however, is not the order of polarity and it appears that other factors should also be operative in the mixed liquid crystal formation. It has been already discussed before in the case of CH_3 and Cl groups that the size of the groups play an important role in mixed liquid crystal formation.

Further, it has been shown by Gray (102) that for a molecule to be mesomorphic it should possess polar groups and the molecule itself should be highly polarizable. It, therefore, appears that the order of efficiency should be a cumulative effect of factors like dipole interactions, overall polarizability of the system, size of the groups, shape of the molecules and even hydrogen bonding and mutual conjugative effects.

Amongst the systems studied in Table 100, there are some isomeric pairs of Schiff's bases with their end groups interchanged from p,p' to p',p positions but there appears to be no significant change towards mixed liquid crystal formation as a result of such an arrangement. The slopes of the transition lines for such isomeric pairs are given in Table 109.

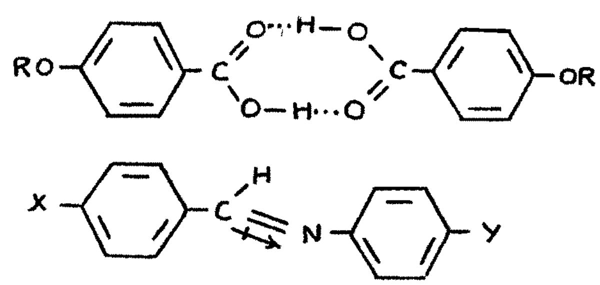
Table 109

No.	Schiff's bases 			Slope of the transition line	Schiff's bases 			Slope of the transition line
1.	OCH_3	CH:N	Cl	9.0	Cl	CH:N	OCH_3	9.0
2.	Cl	CH:N	OC_2H_5	8.3	OC_2H_5	CH:N	Cl	8.3
3.	$N(CH_3)_2$	CH:N	Cl	12.8	Cl	CH:N	$N(CH_3)_2$	12.8
4.	NO_2	CH:N	Cl	7.8	Cl	CH:N	NO_2	7.5

It can be seen that the values of the slopes of the transition lines of different isomeric pairs compare very well. Hence, it should be said that the isomeric compounds cause the same effect on mixed liquid crystal formation.

p-Anisal-p-phenetidine and p-ethoxybenzal-p-phenetidine are monotropic nematic liquid crystals. Mixed liquid crystals of these Schiff's bases separately with the liquid crystalline component p-acetoxybenzal-p-phenetidine are studied in this investigation. In these binary systems (fig. 24,42), the enantiotropic mixed liquid crystalline region is bounded by the area BCDE and beyond the point E, i.e., towards the left hand side of the phase diagram the mixed liquid crystallinity is exhibited in the supercooled state. Such mixtures should form continuous series of enantiotropic and monotropic mixed liquid crystals.

With a view to get a comparative picture of the mode of mixed liquid crystal formation when the liquid crystalline components are different, some non-liquid crystalline Schiff's bases are studied with the liquid crystalline component, p-n-butoxybenzoic acid. Molecules of p-n-butoxybenzoic acid form dimers and as can be seen below, compared to Schiff's bases they possess a more linear structure. The molecules of Schiff's bases, although they possess an essentially linear structure, will have a difficulty in close packing and consequent alignment with the molecules of p-n-butoxybenzoic acid dimers ; as a result steep transition lines may be expected. This is so in several binary mixtures comprising



p-n-butoxybenzoic acid and non-liquid crystalline Schiff's bases in spite of the polar groups present in the non-liquid crystalline molecules. The slopes of the transition lines in such binary systems differ markedly from those obtained from the study of the mixtures of the Schiff's bases individually with p-acetoxybenzal-p-phenetidine. The two values of the slopes of the transition lines are given in Table 110.

Table 110

No.	Substance	Slope of the transition line (p-acetoxy-benzal-p-phenetidine as liquid crystal) (^{o}C/mole %) x 10	Slope of the transition line (p-n-butoxy benzoic acid as liquid crystal) (^{o}C/mole %) x 10
1.	$NO_2.C_6H_4.CH:N.C_6H_4.OC_2H_5$	1.5	5.0
2.	$OCH_3.C_6H_4.CH:N.C_6H_4.OCH_3$	4.0	11.0
3.	$Cl.C_6H_4.CH:N.C_6H_4.OC_2H_5$	8.3	9.0
4.	$OCH_3.C_6H_4.CH:N.C_6H_4.I$	13.0	11.5
5.	$NO_2.C_6H_4.CH:N.C_6H_4.I$	11.5	6.5
6.	$N(CH_3)_2.C_6H_4.CH:N.C_6H_4.OC_2H_5$	6.5	13.0
7.	$NO_2.C_6H_4.CH:N.C_6H_4.Cl$	7.8	5.2
8.	$OCH_3.C_6H_4.CH:N.C_6H_4.Cl$	9.0	11.0

An attempt to derive group slopes in the same way as in the case of binary mixtures of non-liquid crystalline Schiff's bases and p-acetoxybenzal-p-phenetidine is without any success. The same group is found to possess different group slope values and hence no quantitative derivation is possible. The order of group efficiency obtained in the case of isomorphous mixtures of non-liquid crystalline Schiff's bases and liquid crystalline Schiff's base,p-acetoxybenzal-p-phenetidine could not be obtained in this case as the admixed molecules are not isomorphous with the molecules of the liquid crystalline component, p-n-butoxybenzoic acid. However, qualitatively there appears to be no difference in the nature of the mixed liquid crystal formation with p-n-butoxybenzoic acid as the liquid crystalline component.

With a view to have further evidence on mixed liquid crystal formation in mixtures of isomorphous substances, some systems comprising liquid crystalline p-n-butoxybenzoic acid and non-liquid crystalline substituted benzoic acids are studied in this investigation. These non-liquid crystalline substituted benzoic acids are listed in Table 111 alongwith the slopes of the transition lines for the respective binary systems.

The components of these binary mixtures being isomorphous it should be expected that the effects of the end groups would be specific and also additive. The group slope values derived from the slopes of the transition lines are arranged in the order of their efficiency towards mixed liquid crystal formation

Table 111

p-n-Butoxybenzoic acid (nematic liquid crystal)

with

	Slope of the transition line (^{o}C / mole %) x 10
1. p-Nitrobenzoic acid	-
2. p-Ethoxybenzoic acid	-
3. p-Methoxybenzoic acid	2.0
4. p-Chlorobenzoic acid	3.3
5. p-Toluic acid	3.2
6. p-Bromobenzoic acid	3.6
7. p-Iodobenzoic acid	4.6
8. p-Hydroxybenzoic acid	14.5

as under :

End groups	NO_2 >	OC_2H_5 >	OCH_3 >	Cl =	CH_3 >	Br >	I >	OH
Group slopes	-	-	1.0	1.6	1.6	1.8	2.3	7.2

The magnitudes of these group slope values are low compared to those obtained in the study of Schiff's bases with p-acetoxybenzal-p-phenetidine in this investigation, as well as those obtained by Dave et.al. (141,142) in their study of binary systems of Schiff's bases with p-azoxyanisole as a liquid crystal ; the magnitudes of group slope values for NO_2 and OC_2H_5 groups cannot be derived in the usual manner as the transition lines show an upward trend. However, it can be seen that the order of efficiency of the end groups remains the same.

The difference in the magnitude of the group slope values can be ascribed to the fact that in the case of benzoic acid mixtures the two components are quite linear which will contribute to the greater degree of packing between the molecules, compared to the mixtures of Schiff's bases as well as the mixtures of Schiff's bases with p-azoxyanisole. The molecules of Schiff's base compounds and p-azoxyanisole, as can be seen, are not as linear as the benzoic acid molecules and hence it can be expected that the packing of the molecules will not be as compact as in the case of the benzoic acid molecules.

It can, therefore, be said that even if the group slope values may differ in magnitude, such an order of efficiency towards mixed liquid crystal formation should be expected provided the components of such binary mixtures are isomorphous.

Dave (159) and later Dave and Lohar (142) in their studies on mixed liquid crystal formation have reported that compared to the end groups the effect of the central group may be small or negligible.

In the present investigation some compounds having different central groups but the same end groups are studied with p-acetoxybenzal-p-phenetidine, a liquid crystal. The slopes of the transition lines in these cases are given in Table 112.

Table 112

p-Acetoxybenzal-p-phenetidine (liquid crystal)

with

	Slope of the transition line (^{o}C / mole %) x 10
1. $Cl.C_6H_4.CH:N-N:CH.C_6H_4.Cl$	5.5
2. $Cl.C_6H_4.CH:N.C_6H_4.Cl$	14.4
3. $Cl.C_6H_4.CH:CH.CO.C_6H_4.Cl$	18.5
4. $OCH_3.C_6H_4.CH:N.C_6H_4.OCH_3$	4.0
5. $OCH_3.C_6H_4.CH:CH.CO.C_6H_4.OCH_3$	16.0

It can be seen from the values of the slopes of the transition lines that the compound with a central group -CH:N.N:CH- favours most and that with -CH:CH.CO- favours least towards mixed liquid crystal formation, inspite of the presence of the same end groups. However, no generalisation can be made till more such mixtures are studied.

A number of binary systems wherein both the components are non-liquid crystalline substances are also studied in this investigation. Bogojawlensky and Winogradow (132) have observed that mixed liquid crystals are formed in binary mixtures of isomorphous substances, one or both of which may be non-mesomorphic. They found that the transition lines in many cases were sharp and linear ; and by the extrapolation of these linear transition lines they obtained latent or virtual transition temperatures for the non-mesomorphic substances. Vorlander and Gahren (133) also observed the formation of mixed liquid crystals in mixtures of non-mesomorphic substances like anisic acid with piperic acid and cinnamic acid with α-anisalpropionic acid. Dave and Dewar (141) made an attempt but could not obtain mixed liquid crystals in mixtures of p-anisal-p-anisidine and p-anisal-p-toluidine, both of which were non-mesomorphic. They have pointed out that the transition lines are not invariably straight and in that case reliable extrapolation is impossible. The transition lines should be more or less straight if the two components are of similar shape and structure.

Dave and Lohar (143,160) however, obtained enantiotropic mixed liquid crystals in binary systems comprising Schiff's bases and in binary mixtures of p-methoxybenzoic acid and p-ethoxybenzoic acid, wherein both the components are non-liquid crystals.

Walter (134) has explained the appearance of crystalline liquid properties in mixtures of substances which by themselves are not crystalline liquids. The substances which give such mixed liquid crystals, crystallise very well and do not permit under-cooling of their melts. A rather characteristic monotropic crystalline liquid phase which should be expected according to its chemical constitution, remains latent, even if its mesomorphic transition point is not much below its solid crystal melting point. If two such chemically similar substances are mixed the melting points of the solid phases, which are usually lowered compared to the melting points of the pure components, may fall below the mixed melting points of the crystalline liquid phases which lie between the two latent mesomorphic transition points of the pure components. Such a mixture will then form enantiotropically mixed liquid crystals.

In the present study are examined some nine binary systems of Schiff's base compounds, both the components of which are non-liquid crystalline. Out of these, four mixtures are found to exhibit genuine enantiotropic mixed mesomorphism over a range of temperature and concentration (figs. 82,83,84,85).

Table 113

Sys.No.	Binary systems of components A and B.	Range in mole % of component A, over which enantiotropic mixed mesomorphism is exhibited.
I	A. p-Nitrobenzal-p-anisidine B. p-Anisal-p-phenetidine	38.5....51.5
II	A. p-Ethoxybenzal-p-phenetidine B. p-Dimethylaminobenzal-p-phenetidine	44.0....73.0
III	A. p-Ethoxybenzal-p-phenetidine B. p-Anisal-p-phenetidine	21.0....59.0

Table 113 (Contd.)

IV .	A. p-Ethoxybenzal-p-phenetidine B. p-Nitrobenzal-p-phenetidine	27.5....82.5

p-Nitrobenzal-p-anisidine, p-anisal-p-phenetidine, p-ethoxybenzal-p-phenetidine, p-dimethylaminobenzal-p-phenetidine and p-nitrobenzal-p-phenetidine are studied separately with a liquid crystalline substance, p-acetoxybenzal-p-phenetidine (figs. 46,24,42,15,45) and the transition lines are extrapolated. The values obtained for the latent transition temperatures of these non-liquid crystalline substances are 94.5°C, 121.5°C, 143.0°C, 97.5°C and 84.5°C respectively. p-Anisal-p-phenetidine and p-ethoxybenzal-p-phenetidine exhibit monotropy at 121.5°C and 143.0°C respectively ; these temperatures compare well with the latent transition temperatures obtained by extrapolation.

The range over which mixed liquid crystals are formed in such non-liquid crystalline binary systems should normally vary with the overall polarity of the end groups present inthe binary systems. System IV in Table 113 exhibits mixed mesomorphism over a larger concentration range while system I over a concentration range which is least of all. But, in such systems the polarity alone cannot be taken as the only prerequisite to exhibit mixed mesomorphism for, many such binary systems of non-liquid crystalline substances possessing highly polar groups fail to exhibit mixed mesomorphism. The lowering in the melting points in such cases is not reached to a point for the liquid crystalline phase to exist. Further, system II (Table 113) in which the over-all polarity of the end groups is less than in system I, exhibits mixed liquid crystallinity over a wider region compared to that exhibited by system I. Evidently, it appears that besides the polarity of the terminal groups, other factors such as the course of the melting curves, the crystallising tendency of the components in presence of one another and the like should be operative in the formation of mixed liquid crystals in mixtures of non-liquid crystalline substances. The range over which mixed mesomorphism should be exhibited in such mixtures will depend on the over-all efficiency of the system contributed by the molecules of the two non-liquid crystalline components.

A binary mixture of monotropic mesomorphic substances may or may not exhibit enantiotropic mixed mesomorphism over a range of temperature and concentration. A mixture of two monotropic Schiff's bases (system III, Table 113) exhibits enantiotropic mixed mesomorphism over a range of temperature and concentration. Lohar (160) studied such a mixture of two monotropic Schiff's bases viz. p-propionoxybenzal-p-toluidine and p-propionoxybenzal-p-chloroaniline, but could not observe any enantiotropic mixed mesomorphism. However, it should be stated that mixtures of monotropic liquid crystalline substances do exhibit mixed mesomorphism continuously throughout the undercooled region.

It may, therefore, be said that the main factors influencing the appearance of enantiotropic mixed mesomorphism in mixtures of non-liquid crystalline substances are that (i) 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 and (ii) the terminal groups of the non-liquid crystalline substances should be sufficiently polar.

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 coincide with the corresponding values obtained by the extrapolation of the transition lines in mixtures of these non-mesomorphic substances separately with any liquid crystalline component of similar shape and structure. Such a comparison is given in Table 114.

It can be seen from the phase diagrams that the transition lines are slightly curved, even then the values compare well. This indicates that reliable extrapolation for deducing the latent transition

Table 114

No.	Non-liquid crystalline component.	L.T.P °C., extrapolated	
		with p-acetoxy-benzal-p-phenetidine.	in mixtures of non-mesomorphic substances.
1.	p-Nitrobenzal-p-anisidine	94.5	95.0
2.	p-Anisal-p-phenetidine	121.5	121.5
3.	p-Ethoxybenzal-p-phenetidine	143.0	143.0
4.	p-Dimethylaminobenzal-p-phenetidine	97.5	97.5
5.	p-Nitrobenzal-p-phenetidine	84.5	85.0

temperatures of the non-mesomorphic substances as suggested by Bogojawlensky and Winogradow (132), is possible and fairly correct values can be obtained. But it should be emphasized that the extrapolation will be reliable only in the case of binary mixtures having almost linear transition lines, the admixed molecules of which are similar in shape and structure, and wherein the course of the undetermined transition line could be traced by the exhibition of the monotropic mesomorphism in the supercooled melt over a reasonable distance. On the other hand, if the admixed molecules are dissimilar, then the transition lines in such binary systems would be either very steep or would exhibit a concavity; in either case the extrapolation will not be possible.

Walter (134) and Lohar (160) studied the systems of p-methoxybenzoic and p-ethoxybenzoic acids separately with p-methoxycinnamic acid. By the extrapolation of the corresponding transition lines they found the latent transition temperatures for both p-methoxybenzoic acid and p-ethoxybenzoic acid. Lohar (160) further, extrapolated the transition line obtained in the binary mixture of p-methoxybenzoic and p-ethoxybenzoic acids, on either side and obtained agreeable values for the latent transition temperatures of both the acids. During this investigation these two acids are studied separately with another liquid crystalline component, p-n-butoxybenzoic acid and their latent transition temperatures are determined by reliable extrapolation of almost linear transition lines in either case. There is a close agreement between the values of the latent transition points for the two acids obtained in the present investigation, when compared with those obtained by Walter (134) and Lohar (160) as shown in Table 115.

Table 115

Non-mesomorphic component.	L.T.P ^{o}C., extrapolated in mixture with			In mixture of alkoxy benzoic acids.
	p-Methoxy-cinnamic acid. (Walter)	p-Methoxy-cinnamic acid. (Lohar)	p-n-Butoxy-benzoic acid. (Present study)	(Lohar)
p-Methoxy-benzoic acid	155.6	157.5	155.5	156.5
p-Ethoxy-benzoic acid	165.0	169.0	168.5	169.5

This again substantiates the generalisation that the latent transition temperatures could be reliably determined by extrapolation provided the components of a binary system are similar in shape and structure.

Walter (134) and Lohar (160) who studied the mixtures of isomorphous substances calculated the transition temperatures using the following equation based on the law of mixtures.

$$t_m = (t_1C_1 + t_2C_2) : (C_1 + C_2)$$

where t_m is the transition temperature of the mixed melt to be determined, t_1 and t_2 are the transition temperatures of the two pure components and C_1 and C_2 their concentrations in mole per cent. The observed and calculated values of the transition points for the binary systems examined in the present investigation are given in Table 116. As the above equation is based on the law of mixtures, evidently it can be applied where the transition points of the mixtures fall regularly between the two transition temperatures i.e., where the transition lines are straight joining the two transition temperatures. The transition lines for the mixtures examined here are slightly curved and that accounts for the small difference between the observed and calculated values of the transition points. Walter (134) further calculated the latent transition temperature of a substance according to the equation :

$$t_1 = t_2 - \left[100\ (t_2 - t_m) : C_1\right]$$

where t_1 is the latent transition temperature to be sought, t_2 the known transition temperature of an added, chemically similar substance, t_m the transition temperature of such a mixture at concentration C_1 in mole per cent of the non-liquid crystalline component. This formula cannot be applied in the case of the binary systems studied in this investigation, obviously because the transition lines are rather curved. However, these two equations can be applied with good results where the transition lines are straight, as is the case in the systems p-n-butoxybenzoic acid : p-ethoxybenzoic acid and p-n-butoxybenzoic acid : p-toluic acid (Table 117).

Table 116

No.	Component A	M.P. °C.	T.P. °C.	Component B	M.P. °C.	T.P. °C.	Mole % of B	Mixed T.P. t_m observed in °C.	Mixed T.P. t_m calculated in °C.
1.	p-Acetoxy-	118.5	137.5	p-Ethoxy-	148.0	(143.0)	2.44	136.8	137.6
	benzal-p-			benzal-p-			5.21	136.0	137.7
	phenetidine			phenetidine			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

Table 116 (Contd.)

							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)
2.	P-Acetoxy-	118.5	137.5	p-Anisal-	128.5	(121.5)	6.04	136.0	136.5
	benzal-p-			p-phene-			11.33	134.0	135.6
	phenetidine			tidine			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

Table 116 (Contd.)

							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)
3.	p-Ethoxy-benzal-p-phenetidine	148.0	(143.0)	p-Anisal-p-phenetidine	128.5	(121.5)	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

Table 116 (Contd.)

							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)
4.	p-Acetoxy-benzal-p-phenetidine	118.5	137.5	p-Nitro-benzal-p-anisidine	135.0	-	5.52	136.5	135.1
							10.68	135.0	132.9
							16.38	133.4	130.5
							22.53	132.0	127.8
							27.36	130.0	125.7
							32.30	128.0	123.6

Table 116 (Contd.)

							37.09	126.5	121.5
							42.38	124.6	119.3
							47.64	122.5	117.0
							52.57	119.5	114.9
							57.03	117.5	113.0
							62.55	115.0	110.6
							67.28	(112.4)	(108.5)
							72.64	(109.5)	(106.2)
5.	p-Nitro-benzal-p-anisidine	135.0	-	p-Anisal-p-phene-tidine	128.5	(121.5)	39.88	(102.5)	(105.5)
							45.05	(103.5)	(106.9)
							50.05	105.0	108.1
							55.05	106.5	109.6
							57.46	107.4	110.3
							60.10	108.5	110.9
							63.40	(109.0)	(111.8)
							70.00	(111.0)	(113.5)

Table 116 (Contd.)

							72.58	(112.5)	(114.2)
							79.68	(114.5)	(116.3)
6.	p-Acetoxy-benzal-p-phenetidine	118.5	137.5	p-Dimethyl-aminobenzal-p-phenetidine	148.0	-	2.72	135.5	136.4
							5.89	133.5	135.1
							10.40	130.2	133.3
							15.80	128.0	131.2
							18.19	126.0	130.3
							22.46	124.0	128.5
							25.91	122.0	127.1
							31.87	120.0	124.8
							36.83	117.5	122.8
							41.28	116.0	120.9
							47.28	(113.4)	(118.5)
							51.59	(112.0)	(116.8)
							56.07	(111.0)	(115.0)

Table 116 (Contd.)

7.	p-Ethoxy-benzal-p-phenetidine	148.0	(143.0)	p-Dimethyl-aminobenzal-p-phenetidine	148.0	-	5.59	(141.5)	(140.4)
							10.29	(139.6)	(138.2)
							15.76	(138.0)	(135.7)
							18.46	(137.0)	(134.6)
							20.66	(136.0)	(133.6)
							25.94	(134.2)	(131.2)
							30.13	133.0	129.2
							34.60	131.0	127.2
							40.68	129.0	124.6
							44.65	127.0	122.6
							50.13	125.0	120.1
							55.26	123.0	117.8
							60.14	(121.0)	(115.5)

Table 116 (Contd.)

8.	p-Acetoxy-benzal-p-phenetidine	118.5	137.5	p-Nitro-benzal-p-phenetidine	123.5	-	5.34	136.8	134.7
							10.48	136.0	131.9
							14.85	135.0	129.5
							21.43	133.0	126.1
							31.10	129.6	121.0
							35.55	127.5	118.6
							41.34	125.2	115.5
							51.50	120.0	110.3
							60.81	115.6	105.3
							70.82	109.0	99.9
							75.05	(105.5)	(97.8)
							77.10	(104.5)	(96.7)

Table 116 (Contd.)

9.	p-Ethoxy-benzal-p-phenetidine	148.0	(143.0)	p-Nitro-benzal-p-phenetidine	123.5	-	7.08	(141.0)	(138.8)
							10.03	(140.0)	(137.1)
							14.12	(138.5)	(134.8)
							19.89	137.5	131.5
							24.82	135.8	128.6
							29.80	134.0	125.6
							35.58	132.5	122.3
							39.97	131.0	119.8
							44.89	129.0	116.9
							49.64	126.8	114.1
							55.02	123.5	111.1
							59.86	120.5	108.2
							64.60	117.2	105.4
							69.70	113.2	102.6
							74.85	(109.0)	(99.6)
							79.43	(106.0)	(97.0)

Table 117

No.	Component A	M.P. in °C.	T.P. in °C.	Component B	M.P. in °C.	T.P. in °C.	Mole % of B	Mixed T.P. t_m observed in °C.	Latent T.P. t_1 calculated in °C.	Latent T.P. t_1 extrapolated
1.	p-n-Butoxy-benzoic acid	147.0	160.0	p-Ethoxy-benzoic acid	196.0	-	4.96	159.8	156.0	168.5
							11.86	160.4	163.4	
							17.15	160.5	162.9	
							22.62	161.6	167.1	
							28.80	161.8	166.3	
							33.73	162.0	165.9	
							38.99	163.0	167.7	
							43.18	163.5	168.1	
							49.29	164.2	168.5	
							53.63	165.0	169.3	
							65.22	166.0	169.2	
							67.43	166.2	169.1	

Table 117 (Contd.)

2.	p-n-Butoxy-benzoic acid	147.0	160.0	p-Toluic acid	177.0	-	6.11	157.6	120.7	125.0
							13.40	155.0	122.7	
							19.54	153.0	124.2	
							26.92	150.5	124.7	
							32.52	148.5	124.6	
							38.42	147.0	126.0	
							43.43	145.0	125.5	
							48.54	143.0	125.0	
							52.05	141.5	124.5	
							58.81	140.0	126.0	
							62.92	138.0	125.0	

B : MIXED POLYMESOMORPHISM

The binary systems studied so far mainly comprise of components, one or both of which may be nematic liquid crystal or non-mesomorphic. Recently Arnold and Sackmann (172) have done considerable work to test the miscibility of liquid crystalline phases viz. the miscibility of nematic phases amongst one another, nematic phases with smectic phases and smectic phases amongst one another. They have reported that nematic phases of two different compounds are completely miscible and form a homogeneous nematic liquid crystalline region and smectic phases of two different compounds are likewise miscible forming a homogeneous smectic mesomorphic region. However, the smectic phase of one compound and the nematic phase of the other compound are not continuously miscible.

Recently, Dave et.al. (173) have studied mixed smectic mesomorphism in the binary systems where one of the components is a smectic liquid crystal viz. ethyl p-azoxybenzoate and the other a non-liquid crystalline Schiff's base. When the transition temperatures were plotted against the mole per cent of the smectic component, they obtained two general types of curves for the smectic - isotropic transitions : (i) a usual curve where the transition lines are depressed regularly and (ii) a rising curve showing a maximum. The mixed mesomorphism in the smectic phase has been explained as under :

A smectic mesophase is a system of stratified molecular structure where rod-shaped molecules lie parallel in each stratum ; hence, unlike the nematic phase in which the molecules have translational freedom but restricted rotational freedom, the molecules in the smectic phase should have restricted translational and rotational freedom. Another substance dissolved in such a smectic liquid would be in an anisotropic environment and it would affect the properties of the mesomorphic substance in an unexpected manner ; the orientation of the molecules of the mesomorphic substance will be affected to a more or less extent depending on the similarity or dissimilarity of the structure of the solute molecule and the effective dipole moments of its functional groups. Unlike the nematic mesophase, the smectic phase consists of strata of the molecules ; therefore, some of the molecules of the compound dissolved in such a phase can occupy the place between smectic molecules in each stratum and the rest of the molecules may form molecular strata in which the non-mesomorphic molecules in each stratum lie parallel to each other. Such a stratum of non-mesomorphic molecules should pack itself between the two strata of the smectic component and should form a homogeneous smectic melt. It has been suggested that very high dipole moment due to $C-NO_2$ link present in the non-mesomorphic component acting in the direction of the long axis of the molecule, not only favours such a smectic mixed liquid crystal formation but also raises the smectic thermal stability to a considerable extent compared to the smectic thermal stability of the pure smectic component. Such binary systems have been found to exhibit a maximum in their transition curves. They further report that no order of efficiency of the terminal groups, towards mixed mesomorphism could be obtained for the mixed smectic phase as in the case of mixed nematic phase, because the transition lines are curved.

No work seems to have been done to study the effect of dissolution of a non-liquid crystalline substance in a liquid crystalline component exhibiting both smectic and nematic phases. Hence, some binary systems of this type, where a polymesomorphic substance, p-n-dodecyloxybenzal-p-n-butoxyaniline, which exhibits both smectic and nematic phases is admixed with non-mesomorphic Schiff's bases, are studied here and listed in Table 118.

Compounds 2 to 8 are non-mesomorphic i.e., they do not exhibit enantiotropic or monotropic mesomorphism, while compound 1 (Table 118) is a monotropic liquid crystal. The polymesomorphic substance, p-n-dodecyloxy-benzal-p-n-butoxyaniline selected in the present study, first melts to a smectic phase at 101.0°C and transforms to a more mobile nematic phase at 111.0°C, finally becoming a clear liquid at 111.5°C. These changes are

Table 118

Component A : p-n-Dodecyloxybenzal-p-n-butoxyaniline

(a smectic - nematic liquid crystal)

mixed with

Component B : a non- liquid crystal

1. p-Anisal-p-phenetidine
2. p-Anisal-p-anisidine
3. p-Dimethylaminobenzal-p-phenetidine
4. p-Anisal-p-chloroaniline
5. p-Anisal-p-bromoaniline
6. p-Nitrobenzal-p-phenetidine
7. p-Nitrobenzal-p-chloroaniline
8. p-Nitrobenzal-p-bromoaniline

quite reversible and before crystallisation, it exhibits one other monotropic smectic phase at 95.0°C. A non-mesomorphic substance dissolved in such a liquid should affect the chemical and physical properties of both the smectic and nematic mesophases in an interesting manner. Just as the word 'mixed mesomorphism' is coined for the liquid crystalline state exhibited by a binary mixture comprising either a nematic or smectic mesomorph, the term 'mixed polymesomorphism' can be conveniently used here.

In the nematic binary mixtures where one component is a nematic liquid crystal and the other a non-liquid crystal, one general type of phase diagrams is obtained where the nematic - isotropic transition lines are regularly depressed. In the binary mixtures studied in the present investigation comprising one polymesomorphic component and the other non-mesomorphic component, when the solid - mesomorphic, mesomorphic - mesomorphic and mesomorphic - isotropic transition temperatures are plotted against the mole per cent of the polymesomorphic component, two distinct types of phase diagrams are obtained : (1) a phase diagram having two transition curves ; the lower one showing the smectic - nematic transition and the upper one marking the mesomorphic - isotropic transition (fig. 91) and (2) a phase diagram possessing a single smectic - isotropic transition curve exhibiting a maximum (fig.96).

In the case of the phase diagrams of the binary systems of the first type, the nematic -isotropic transition temperatures lie on a regularly depressing curve. The transition lines are almost linear and are comparable with those obtained in the study of mixed mesomorphism in a pure nematic phase. The smectic-nematic transition temperatures in these systems also lie on a regularly falling curve ; the curve falls gradually in the phase diagrams of the binary systems where it cuts the melting point curve to the left of the eutectic (fig. 92) and falls rather steeply when it cuts the melting point curve to the right of the eutectic (fig.91). The phase diagrams of the first five binary systems (Table 118) reveal that the nematic phase region increases at the cost of the smectic phase region, as the concentration of the non-mesomorphic component increases. This may be ascribed to the change taking place in the molecular arrangement of the smectic mesophase due to the movement of the molecules in the direction of their long axes. At this stage the molecules are slipping out of the characteristic layers of the smectic phase but remain parallel to one another in spite of their end positions being disturbed, thus giving a nematic phase. As the concentration of the non-mesomorphic component increases, a stage is reached when the lateral intermolecular cohesions are weakened so much that the smectic phase altogether disappears and the solid mixture passes directly into the nematic phase.

In the case of the phase diagrams of the binary systems of the second type the smectic-isotropic transition curve exhibits a maximum. It is interesting to note that in such systems the nematic phase present in the pure p-n-dodecyloxybenzal-p-n-butoxyaniline is completely eliminated by the addition of the non-mesomorphic nitro- compounds and the solid mixture passes directly into pure smectic phase which in turn transforms to isotropic liquid. This elimination of the nematic phase may probably be attributed to the high dipole moment of the NO_2 group present in the non-mesomorphic component, which favours most for the smectic mixed mesomorphism just like the formation of polymesomorphism of the smectic phases in 4'-n-alkoxy-3'-nitrodiphenyl-4-carboxylic acids (116) and the absence of the same phenomenon in 4'-n-alkoxydiphenyl-4-carboxylic acids (111). The enhanced smectic thermal stability observed in these systems demands an explanation. Gray and Byron have explained the enhanced smectic thermal stability of 4-p-n-nonoxybenzylideneamino-4'-chlorobiphenyl in which the terminal C-Cl dipole moment acts parallel to the major molecular axis, by assuming that the molecules are tilted at an angle to the layer interfaces (102). By the tilting of the molecules away from the perpendicular arrangement, the separation of the positive and negative charges of C-Cl dipoles does not necessarily increase but the 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 attraction and the smectic properties. Now, in the mixtures studied here, the liquid crystalline component has three dipole moments, two arising from the terminal alkoxy groups and another from the central -CH=N- group. These dipole moments act at an angle to the main molecular axis. However, at least one dipole moment due to $-NO_2$ group present in the non-mesomorphic component acts parallel and the other may act at an angle to the major molecular axis. In some cases, both the dipole moments of the terminal groups may act parallel to the major molecular axis. To account for the enhanced smectic properties of the binary mixtures comprising non-mesomorphic component which possesses terminal groups of high dipole moment e.g., $-NO_2$, the molecular strata formed in the smectic melt should be tilted at an angle to the planes of the smectic strata where the net energy of attraction should become effective to enhance the lateral cohesions and the smectic properties. The extent to which the smectic - isotropic transition temperature is raised, should therefore, depend upon the molecular constitution of the non-mesomorphic component and the direction , and the magnitude of the dipole moments of the terminal groups. All the nitro-compounds studied here in mixture with p-n-dodecyloxybenzal-p-n-butoxyaniline, exhibit a maximum.

It should be stated here that no definite order of efficiency of the terminal groups towards mixed mesomorphism either in the nematic or the smectic phase could be derived from the present study of mixed polymesomorphism.