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Emergence of Smectic Mesophase in Binary Mixtures of Pure Nematogens

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Binary mixtures both components of which are liquid crystals are known to form continuous mixed liquid crystals.[1] Most of them do not undergo any change in their mesomorphic textures, though a few have been found to give rise to different textures.[2] We report here a binary system consisting of (A) *p*-nitrophenyl-*p′*-*n*-amyloxycinnamate (90.5–120.5°) and (B) *p*-methoxyphenyl-*p′*-*n*-heptyloxycinnamate (91.0–120.5°) which transforms the original nematic texture into a mixed smectic A texture over a range of temperature and concentration. Both components individually are nematic liquid crystals. In their binary mixtures, a two dimensional more ordered mixed Smectic A mesophase emerges between 5.0–92.5 mol% of *p*-methoxyphenyl-*p′*-*n*-heptyloxycinnamate over a temperature range of about 50–105° at its maximum. The mixed smectic-nematic transition curve shows a marked rounded concavity, extrapolation of which on either side yields values of latent transition temperatures 77.0° and 66.5° for the components A and B respectively which could be real in case they were to show polymesomorphism. These values are comparable with those obtained from the study of their homologous series.[3] Besides this unique phenomenon of emergence of the mixed smectic A mesophase out of a mixture of two purely nematic substances, the nematic mesophase also persists continuously in the phase diagram over a range of temperature an concentration. The results are interpreted to account for the unique display of the molecular forces which make such an emergent mixed smectic phase possible.

INTRODUCTION

Physical as well as optical characteristics of individual mesogens may or may not undergo modifications in their mixtures. The trend of modifications, however, would become a characteristic by itself sometimes, if not always, and therefore the study of mixtures of such substances assumes importance. Binary mixtures, none, one or both components of which were liquid crystals[1,4-6] have been studied in sufficient detail over the years and the findings have been quite interesting and enlightening. Emergence of mesophase where none existed, increase or decrease or decrease of the mixed mesomorphic ranges and thermal stabilities and the study of the factors that influence the modifications are some of the aspects which have received greater attention. Application of DSC and DTA methods to the study of mixed mesomorphism[7] have also revealed several interesting features that were otherwise not discernible, making the study more perfect. Yet, instances where a change in the mesomorphic texture occurs due to the mixtures, are quite rare.[2] We report a similar rare case but one of transformation from the lower order to the higher order of mesomorphism.

EXPERIMENTAL

Synthesis

1. *p-n-Alkoxybenzaldehydes* where the alkoxy groups are —OC_5H_{11} and —OC_7H_{15} were prepared from *p*-hydroxybenzaldehyde.[8]

2. *trans p-n-Amyloxy and heptyloxycinnamic acids* were synthesized from *p-n*-amyloxy and heptyloxybenzaldehydes respectively.[9]

3. *trans p-n-Amyloxy and heptyloxycinnamoyl chlorides* were synthesized from trans *p-n*-amyloxy and heptyloxycinnamic acids respectively.[10]

4. *p-nitrophenyl-p′-n-amyloxycinnamate: p*-nitro phenol (0.01 mol) was dissolved in pyridine (10.0 ml) and was added slowly to the trans-*p-n*-amyloxycinnamoyl chloride (0.015 mol). The mixture was warmed while shaking for an hour and was allowed to stand overnight. It was acidified with cold dilute hydrochloric acid and the precipitates were collected by filtration and were washed with water. The precipitates were further washed with cold dilute sodium hydroxide solution followed by water. The ester obtained was crystallized from ethyl acetate : ethyl alcohol (20 : 80) mixture. The elemental analysis conforms with the calculated ones.

5. *p-methoxyphenyl-p′-n-heptyloxycinnamate: p*-methoxyphenyl-*p′*-*n*-heptyloxycinnamate was similarly synthesized from *p*-hydroxyanisole (0.01 mol) and trans-*p-n*-heptyloxycinnamoyl chloride.

TABLE I

Transition Temperatures (°C)
Binary System: *p*-nitrophenyl-*p'*-*n*-amyloxycinnamate;
p-methoxyphenyl-*p'*-*n*-heptyloxycinnamate

Mol% of *p*-nitrophenyl-*p'*-*n*-amyloxycinnamate	Transitions (°C)		
	Smectic	Nematic	Isotropic
100.00	—	90.5	120.5
95.16	(82.0)	84.5	117.5
90.37	81.5	87.5	116.0
80.60	70.5	94.5	116.0
70.76	63.5	101.5	120.0
60.88	55.5	104.0	119.0
50.90	52.0	105.0	120.0
40.86	51.0	100.5	119.5
30.74	53.0	95.0	121.0
20.56	63.5	87.0	120.0
10.28	73.0	76.5	117.5
05.17	(71.5)	82.5	118.5
00.00	—	91.0	120.5

Sintering rounded minimum touching at 50.5°. Values in the parenthesis indicate monotropy.

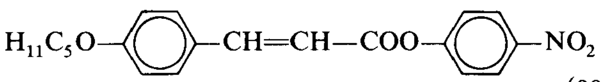
STUDY

The mesomorphic characteristics were studied by the optical method[4] as well as under the polarizing microscope using Kofler heating stage. The transitions are recorded in Table I.

RESULTS AND DISCUSSION

The components comprising the binary system are *p*-nitrophenyl-*p'*-*n*-amyloxycinnamate (A) and *p*-methoxyphenyl-*p'*-*n*-heptyloxycinnamate (B). Both have identical molecular core geometry with two benzene rings bridged by a vinylcarboxy central group, as depicted below:

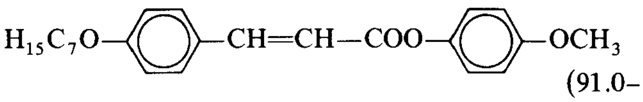
A.



(90.5–120.5°C)

+

B.



(91.0–120.5°C)

The terminal groups, however, differ in size and in the contribution they make to the molecular forces. The molecular forces due to the core structure and the central bridge are of the same magnitude in both moieties. Yet the over all play of molecular forces differs to a certain extent due to the varying terminal groups. While the right hand terminal groups —NO_2 (A) and —OCH_3 (B) are highly polar, endowing the molecules with great terminal attractions, the left hand alkoxy groups —OC_5H_{11} (A) and —OC_7H_{15} (B) contribute to the overall polarizability of the molecules— that of B differing by two more methylene units. These two terminal groups differ in length proportionately and cause the ratios of length to breadth as well as of lateral to terminal attractions to differ too. Both mesogens are nematogens of almost equal phase length, say of 30 °C. Since the core geometry of the moieties of both is identical with over all terminal attractions differing only a little, the binary mixtures of these nematogens should be expected to yield a linear behaviour for the upper transition boundary curve besides formation of continuous mixed liquid crystals.

Besides the system living up to the expectations, it gives rise to a very interesting panorama and yields some unexpected results. The mixed nematic–isotropic transition curve (Figure 1) runs almost parallel to the abscissa though the curve is wavy in parts at the initial concentrations of each other in the mixture at either side and deviates only slightly from the linearity criterion, the maximum deviation being not more than 4 °C on one side (A) and just around 2 °C on the other (B). The solid–mesomorphic transitions for the mixtures depress appreciably on both sides giving a sort of incipient minimum where the eutectic point is expected to emerge. This is a striking feature since in most binary systems the eutectic is well defined. The rounded minimum is obtained with 45 mol% composition of the component A at about 50 °C. While the mesomorphic phase range of the individual components is of about 30 °C, the mixed mesomorphic range is beautifully enhanced throughout the phase diagram reaching the maximum of about 70 °C at 45 mol% concentration of the component A.

But what is more striking and fascinating is the emergence of another mesophase in the mixture system transforming a part of it into a polymesomorphic region in the phase diagram. A binary mixture system of nematogens which are known to exhibit one dimensional orientation gives rise to a two dimensionally ordered smectic mesophase texture over a wide range of temperature and concentration—a phenomenon of rare occurrence. While the mixed nematic mesophase is not eliminated at any stage, the smectic mesophase

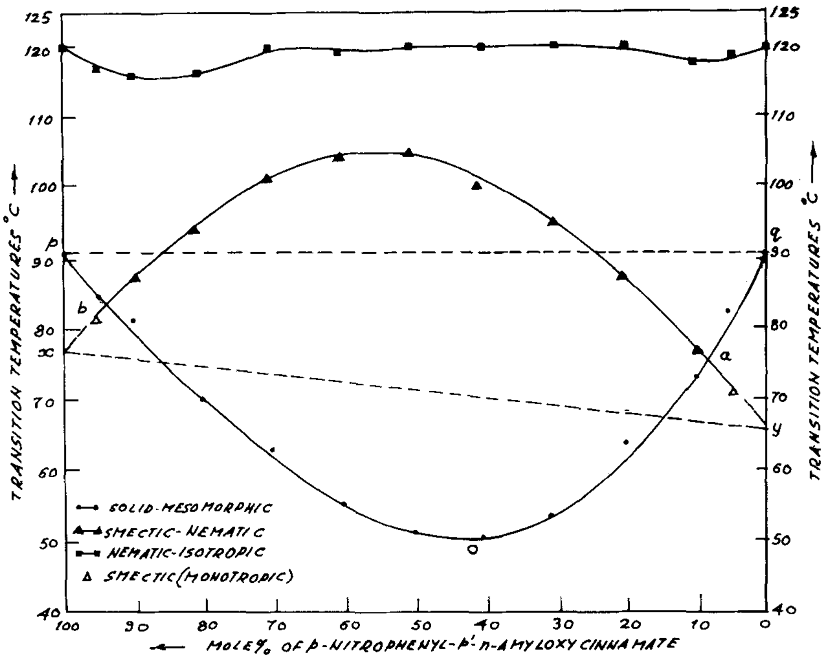


FIGURE 1

makes its appearance between 9.0 and 94.0 mol% of *p*-nitrophenyl-*p*'-*n*-amyloxycinnamate (A). The smectic–nematic transition curve shows a convex nature with a maximum with the result that the mixed nematic mesophase is decreased while the emergent smectic mesophase is enhanced with increasing concentration of the component A, reaching the maximum at about 51 mol% composition, beyond which again the emergent smectic mesophase is progressively decreased. It is noteworthy to observe that with just 9 mol% of A or 6 mol% of B mixed with the other, the more ordered smectic mesophase, out of a mixture of two nematogens, emerges and becomes stronger as the composition is increased. It seems that the lateral attractions are too weak to resist thermal agitation and exhibit a smectic mesophase at the predicted latent smectic transition temperatures 77 °C (A) and 66.5 °C (B) respectively and that the terminal attractions are sufficiently strong to offer resistance to the thermal break down process and favour formation of one dimensionally oriented nematic fluid at higher temperature i.e. 90.5 °C and 91.0 °C respectively. This situation is altered considerably by just 6 mol% or 9 mol% addition of the other to the first, and what was missed in the individual component is gained with a marginal admixture of the other. But the gain is more than anticipated. By joining the two smectic latent transition temperatures of the two components, a hypothetical transition curve showing a hypothetical equilibrium between the probable smectic and nematic mesophases at it could be constructed (Figure 1) and since the solid–mesomorphic transitions of several compositions of these two components lie below this hypothetical curve, smectic mesophase should emerge. Though the lateral adhesions of the individual components are not of the level of being practically effective, their magnitude is not that small either, and that it falls short of the effective level only marginally. Therefore, with a little less than 10 mol% addition of the other component, the lateral adhesions grow and show their force by the emergence of the layered fluid. Obviously, with increasing concentration of the other, the force of lateral adhesions will also grow. But that the force grows beyond the hypothetical transition curve is surprising.

The component with more lengthy alkoxy chain by two methylene units (B) provided added lateral adhesions by its 6 mol% addition to the component A, while the component A is needed to the extent of 9 mol% for strengthening the lateral adhesions of the component B. It is observed that two methylene units make a difference of about 3 mol% in terms of bringing the magnitude of lateral adhesions to the level of being effective for smectic mesophase to appear. Greater length of the alkoxy terminal chain endows the molecules with greater polarizability which strengthens the lateral adhesions. It is further noteworthy that for about every 10 mol% addition of the other component, before the curve acquires the tendency of levelling off, the emergent mixed smectic mesophase length is enhanced by about 8 °C on an average, almost to the same extent the mixed nematic mesophase is decreased.

Intake of thermal energy, after a certain level, may be just enough to predominate over the lateral adherence capacity with the result that a two dimensional smectic mesophase order yields to a one dimensional orientation at the transition of S–N. The amount of thermal energy needed will depend upon the strength of the lateral adhesions; the greater the lateral adhesions the greater the amount of thermal energy needed for the purpose. Now, in the case of the mixtures of these two almost identical substances, the increasing composition of the other induces greater overall polarizability since the number of species of the other component are increased, hence lateral adhesions grow and greater amount of thermal energy would be needed to break their order and transform it to a one dimensional nematic fluid. This (Figure 1) is the case as one proceeds with increasing concentrations of the other from both sides reaching optimum at 51–49 mol% combination. The smectic–nematic transition curve thus shows the nature of maximum deviating from the ideal linear behaviour. The layers perhaps possess greater surface energy in the pile needing greater thermal energy for the transformation of the layered to the threaded texture. It appears that in the mixtures, the contact angle of the layers tends to be nil as the concentration from either side increases with the result that greater force is required to destroy the layered orientation. Though a quantitative evaluation is ruled out at this stage, the factor of the contact angle seems to be quite important and the nature of maximum may find an explanation in it.

Since the solid–mesomorphic transitions sink below the hypothetical curve '*xy*', obtained by joining the latent solid–smectic transitions of the two components (Figure 1), the maintenance of the smectic mesophase up to this curve is rather natural once the combination of molecular forces would be so conducive as to the emergence of a smectic mesophase out of a mixed system of pure nematogens, which is of about 21°C length at its highest. But when the mixed emergent smectic mesophase is found to be exhibited far beyond this hypothetical curve boundary, the strength of adhesions of layers is certainly a matter to receive a more serious consideration. On a qualitative basis again, the hypothetical curve '*pq*' obtained by joining the solid–nematic transitions of the two pure nematogens in question, prescribes another logical limit for the existence of an emergent mixed smectic mesophase on the presumption that the smectic–nematic transition curve may follow the linearity principle. This limit in terms of the phase length is of about 19°C. But in fact, the emergent mixed smectic mesophase transgresses far beyond this limit by about another 15°C at the maximum point. In a general over all manner, the extended smectic mesophase length is about 34°C beyond a normal ideal expectation, which speaks of an equivalent energy needed to disperse the layered structure. In other words, the adhesion power is that high and could find a correlation to the contact angle of the smectic layers that gives rise to interfacial tensions. With the increasing proportions of both components, the contact angles may be tending to be nil which would then necessiate a higher energy for detaching the layers.

In the case of the mixed nematic mesophase, the threaded texture does not give rise to interfacial contacts; therefore the concept of contact angle cannot hold good in this consideration. The end to end adherence capacity, however, does not seem to alter much with the increasing proportions of the other since the terminal attractions will remain intact. At the left end of the phase diagram, nevertheless, the addition of the component B introduces in the fluid the methoxy terminal group which is slightly less polar than the nitro terminal group of the first component. With this change, the packing of the molecules in the orientation seems to be disturbed somewhat which could be the cause of slight depression in the nematic–isotropic transitions. But as the proportion of the methoxy terminal group is increased progressively, the little bit odd packing situation clears up and the transitions get levelled off. When a non-mesomorphic long linear molecule having nitro terminal group at one end is mixed with another equally linear and long molecule having mesomorphic property, the nematic–isotropic transitions are depressed[4-6] a great extent due to dipole–dipole interactions. The transition curve shows a tendency of a rounded minimum; in this binary system also a similar tendency is seen at the left end. And at the right end of the phase diagram also the tendency for an incipient minimum, though of a much lesser degree, is discernible.

A binary system of two Schiffs bases one of which was a monotropic liquid crystal and another a non-liquid crystal[11] gave enantiotropic mixed nematic liquid crystal phase of very good range. In that system, the nematic–isotropic transition curve showed a maximum deviating a good deal from linearity behaviour. Linearity of the transition curves is almost a common feature in most of the binary systems consisting of Schiffs bases, and others too, provided the components have almost an identical molecular geometry. While the maximum shown in the case of the binary system[11] cited above was in the case of emergent mixed nematic mesophase, the present case is for the emergent mixed smectic mesophase. Since the Schiffs bases lack in sufficient lateral adhesions on account of lesser polarizability of the molecules, the binary system of the Schiffs bases[11] did not give rise to a smectic mesophase prior to the mixed nematic mesophase. However, with sufficient length of the molecules, the terminal attractions also were high because both —NO_2 and —OC_2H_5 groups are highly polar, the emergence of the mixed nematic phase could be linked to them.

p-Nitrophenyl-*p*′-*n*-amyloxycinnamate and *p*-methoxyphenyl-*p*′-*n*-heptyloxycinnamate belong to two different homologous series in which the very next members i.e. the sixth and the eighth members respectively are smectogens.[3] It may be said that both these compounds thus lack in lateral adhesions only a little bit individually, but as soon as a mixture of theirs is made, the deficiency of lateral adhesions is made up and the mixed smectic mesophase emerges transforming the system into a polymesomorphic one.

TABLE II

Latent Transition Temperatures

Homologue	LTT for smectic (from mixed study) °C	LTT for smectic (from the homologous series) °C
A	77.0	78 °C
B	66.5	65.5

Extrapolation of the smectic–nematic transition curve on either side yields values for the latent transition temperatures for the smectic mesophase to appear if the conditions could be so conducive, which are in agreement with those obtained from the graphs of the individual homologous series.[3]

The extrapolation is made more reliable because of the monotropic smectic transitions obtained at 96 mol% and 4 mol% of the component *p*-nitrophenyl-*p'*-*n*-amyloxycinnamate on the left and the right sides of the solid–mesomorphic transition curves respectively, supporting our view regarding the reliability of the extrapolation method.[6] Another quite interesting observation discernible is that had the solid–mesomorphic transition curve not shown the tendency of a rounded minimum, and retained the usual nature of the eutectic, the temperature at which the eutectic could have appeared would have been in the vicinity of 40 °C—the upper periphery of ambient temperature range. A third suitable component could reduce this temperature by a further 15–20 °C, giving a mesomorphic mixture at ambient temperature range.

Had the mixed nematic–isotropic transitions depressed giving rise to a concave type of transition curve the possibility of its disappearance at the middle sector of the phase diagram could not be ruled out, though in such eventuality a definite region of mixed nematic liquid crystals at either end would always be expected to be present.

Another interesting feature is the fact that the component B of the binary system which has a methoxy group attached at the right terminal has wider nematic mesophase range than that of the component A where the corresponding terminal group is nitro, while the nematic–isotropic transitions of both are almost the same.

This trend is maintained in the mixed system also, however, with a difference. The smectic–nematic thermal stabilities on the side where the methoxy component predominates are lower than those of the other side where the nitro compound predominates. Nitro with high dipole–dipole interaction would raise the smectic–nematic thermal stability. This results, in keeping with the original individual trend, into somewhat narrower nematic mesophase range on the A side of the phase diagram than that of the B side. Moreover, the initial slope of the nematic–isotropic transition curve on the B side is less than that of the A side. The lesser initial slope on the B side is due to the added nitro compound while that on the A side is due to the added methoxy compound. While the actual values might differ, the qualitative difference in the order of the "slope values" for these two nitro and methoxy groups is comparable with those obtained earlier.[12]

Two binary systems consisting of a smectogen and a non-mesogenic Schiffs base compound have been studied[2] in which formation of mixed nematic mesophase, on about 14 mol% addition of the non-mesogenic Schiffs base in one case and about 10 mol% addition in the other case, has been discerned—the Schiffs bases being different in these systems while the smectogen is the common compound. As per the study, the smectic property is altogether eliminated and its place is taken up by the mixed nematic orientation. The smectogen is a polymorph with two smectic (A and B) variations. Both smectic varieties simply disappear, though, since the mixtures between 1–14 or, 1–10 mol% of the Schiffs bases respectively do not seem to have been studied, it is hard to say if the smectic mesophase was really eliminated altogether. It is probable that for some initial mole-percent composition of the Schiffs bases, one or both variations of smectic mesophase might still be exhibited. The core molecular geometry of all these three Schiffs base compounds is quite comparable with the two nematogens which form the present binary system. Therefore it is tempting to compare the present binary system with them on account of a contrast in their mesomorphic characteristics. In the reported binary system a smectic mesophase is witnessed to be converted into a nematic one while the present binary system yields an emergent smectic mesophase maintaining the original nematic mesophase giving rise to a polymesomorphic character. Since the two binary systems consists of Schiffs bases with $—Cl$, $—CH_3$, $—OCH_3$ and $—OC_4H_9$ terminal groups, the mesomorphic characteristics of these, if any, could be only non-mesogenic except the Schiffs base with butoxy, $—OC_4H_9$ group where the expected mesophase could be smectic on account of added polarizability. Again since in their mixtures the over all polarizability is decreased on account of the presence of the non-mesomorphic Schiffs bases, the original smectic mesophase of the smectogen, after a certain composition of the non-mesogenic Schiffs base, would be tending to disappear. At the same time on account of the sufficiently polar $—OCH_3$ group of the nonmesogenic Schiffs bases, the probability for a nematic orientation is the most expected one in mixed conditions. Therefore, while the smectic force is tending to disappear, the nematic one is emerging on account of the depression experienced in the transitions of the mixed system. While this is so for the two binary systems reported, the components of the present binary system are such as to be originally polymesomorphic, but on account of a slight off balance of the molecular forces they remain nematics only. But in their mixtures, the smectic force is strengthened enough to be realized in the layered structural form in the fluid condition, therefore the latent smectic mesophase emerges as real in the mixtures as discussed above. Since the terminal attractions remain powerful enough, beyond the smectic transition, the nematic property is retained in tact. These binary systems, though rare, indicate the importance of the delicate play of the molecular forces which influence the exhibition of two or one dimensional orientations in the fluid condition.

To summarize, firstly, the possibility of obtaining a higher ordered oriented liquid out of a mixture of less ordered nematogens has been well accredited by this study. Secondly, it is demonstrated that the emergent mixed smectic mesophase length is about four times the phase length of the mixed nematic mesophase. Thirdly, while formation of mixed smectic liquid crystal is on account of display of greater lateral force, the maximum convexity shown by the emergent smectic–nematic transition curve has a direct bearing to the greater requirement of thermal agitation to dislodge the layered texture probably due to the contact angle of the smectic–smectic interface tending to be nil, as the composition is increasing from both sides, thereby giving rise to a condition of maximum adhesion energy opposing the thermal agitation. Fourthly, nematogens whose lateral attractions fall short of the required level by a marginal magnitude will have the greater potential of exhibiting a smectic mesophase in their mixtures provided, however, that the nematogens in questions have almost identical core molecular geometry. By the same logic, it could be said that smectogens which have sufficient terminal attractions otherwise, may be expected to give rise to a nematic mesophase in their mixtures. Thus from binary mixtures of monomesomorphic substances, polymesomorphism may emerge if the conditions would be conducive in a manner as revealed by the present system. Fifthly and lastly, the extrapolation method of determining latent transition temperature is beyond doubt quite reliable and that their determinations are fruitful in many ways.

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