Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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To cite this article: R. A. Vora & Nilesh Dixit (1984): Mixed Mesomorphism: Binary Liquid Crystal Systems Exhibiting Linear and Non-Linear Thermal Behaviour, Molecular Crystals and Liquid Crystals, 104:3-4, 249-256

To link to this article: http://dx.doi.org/10.1080/00268948408070427

Mol. Cryst. Liq. Cryst., 1984, Vol. 104, pp. 249–256
0026-8941/84/1044-0249/$18.50/0

Mixed Mesomorphism: Binary Liquid Crystal Systems Exhibiting Linear and Non-Linear Thermal Behaviour†

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(*Received February 28, 1983; in final form September 13, 1983*)

The number of binary systems are studied where one of the component is 4-Nitrobenzylidene-4′-*n*-heptyloxyaniline, which is polymesogenic exhibiting enantiotropic nematic and monotropic smectic mesophases. In all the systems studied the second component is either a Schiff base or an ester. Two distinct trends are observed in these binary systems. When the second component possesses a strongly polar nitro terminal group the phase diagrams exhibit linear behaviour. However, the systems where the second component does not possess a strongly polar terminal group, the phase diagrams exhibit non-linear behaviour. In one of such binary system maxima is observed for smectic as well as nematic mesophases and an induced smectic mesophase is also observed. The monotropic smectic and nematic mesophases become enantiotropic even with small percentage concentration of either components in couple of the binary systems. The latent transition temperature is obtained by extrapolation method in one binary system. The UV and IR spectral study was carried out for examining the possibility of charge-transfer complex formation in the binary systems.

INTRODUCTION

Many binary systems are reported which exhibit mesomorphic-isotropic transition temperatures which are linearly dependent on composition. However, Dave *et al.*[1] and Schroeder *et al.*[2] have reported non-linear behaviour in the binary systems where one of the compo-

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†Presented at the Ninth International Liquid Crystal Conf., Bangalore, 1982.

nents has terminal nitro group. In both cases reported above the smectic mesophase is enhanced. Sackmann and Demus[3] reported non-linear behaviour for some mixtures when one component was a chloro mesogen. Recently number of workers have studied binary systems where one of the component has a strongly polar nitro or cyano terminal group.[4-8] They have observed non-linear behaviour in all such systems. They have tried to explain this behaviour by proposing different structures including the possibility of charge transfer complex formation. Domon and Billard[9] have reported binary systems exhibiting non-linear behaviour where none of the components had strongly polar terminal group. Labes *et al.*[10] and Modityaya *et al.*[11] have reported the induced smectic mesophases in the binary systems studied by them. In the present study to evaluate the effect of a strongly polar terminal group, two types of the systems are studied. In both the systems one of the component is a polymesogen having a strongly polar terminal substituent whereas second components are varied, they are mesogenic in the first type and non-mesogenic in the second type of the system.

EXPERIMENTAL

1. Preparation of compounds:

Following compounds were synthesized by known methods. The melting points and transition temperatures agree well with the literature.

(a) 4-Nitrobenzylidene-4′-*n*-heptyloxyaniline.[12]
K 60.0 N 80.0 I (57.0S)

(b) 4(4′-*n*-Heptyloxy benzoyloxy)toluene.[13]
K 58.0 I (53.0 N)

(c) 4-Nitrobenzylidene-4′-*n*-Octyloxyaniline.[12]
K 65 S 79 N 87 I

(d) 4-Methoxybenzylidene-4′-toluidines.[14]
K 95.0 I

(e) 4-Nitrobenzylidene-4′-ethylaniline
K 88.0 I
(Elemental analysis of (e) was satisfactory)

2. Preparation of mixtures:

Both the components were weighed accurately in known proportions and were thoroughly mixed by melting them together in a fusion tube to obtain homogeneous mixture. The melt was quenched and solid obtained was ground and used for determining transition temperatures.

3. Transition temperature determination:

The transition temperatures were determined by using a polarizing microscope equipped with a FP-2 hot stage. Two phase region is not observed in most of the systems having Schiff bases as both the components of the binary system. For the system 1a, two phase region was observed for a very narrow range of temperature and for simplification the highest temperature is recorded.

RESULTS AND DISCUSSION

Binary system type I: Polymesogen + Mesogen/Polymesogen:

System Ia:
Component *A*: 4-Nitrobenzylidene-4′-*n*-heptyloxyaniline
Component *B*: 4(4′-*n*-Heptyloxybenzoyloxy) toluene.

The phase diagram is obtained by plotting mole percent composition of component *A* versus transition temperatures (Figure 1). The monotropic smectic phase of component *A* becomes enantiotropic when mole percent concentration of component *B* is about 15%. The nematic–isotropic transition temperatures also exhibit rising tendency as the concentration of component *B* is increased. However, after showing a maxima at the 79 mole percent concentration of component *B*, it levels off. On the left hand side of the phase diagram it can be seen that only with 20 mole percent concentration of component *A*, the monotropic nematic mesophase becomes enantiotropic and the commencement of monotropic smectic phase begins.

The additional smectic mesophase is observed up to about 40 mole percent concentration of component *A*. As the amount of component *A* increases the smectic mesophase thermal stabilities indicate rising tendency exhibiting maxima at the 70 mole percent concentration of component *A*. The phase transition lines for smectic–nematic as well as nematic–isotropic transition lines exhibit non-linear behaviour. The texture of the smectic mesophase obtained throughout the phase diagram is either focal-conic or fan-shaped. However, the additional smectic phase observed in the phase diagram has a typical texture which can be defined as Schlieren texture.

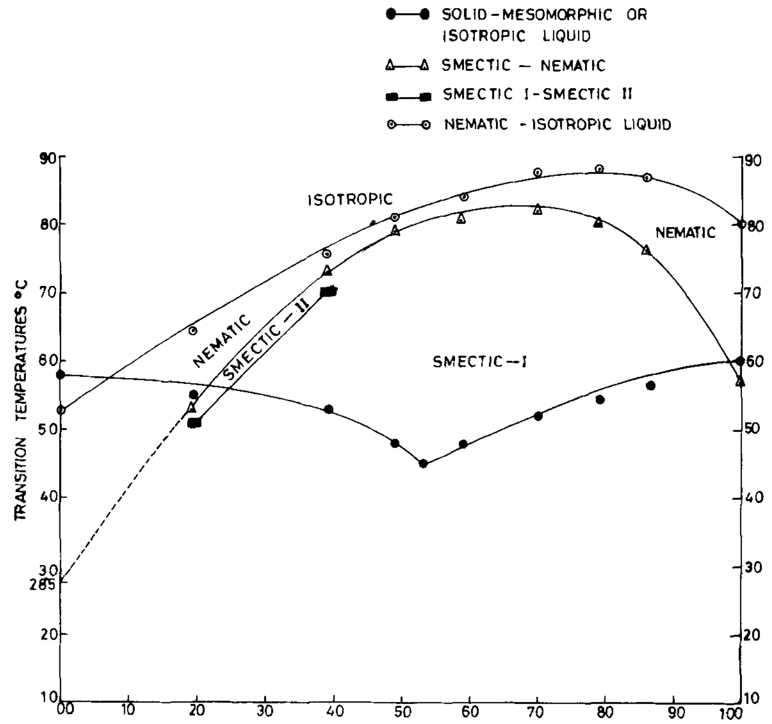

FIGURE 1 System Ia: mole % of 4-nitrobenzylidene-4′-*n*-heptyloxyaniline. 4-Nitrobenzylidene-4′-*n*-heptyloxyaniline: 4(4′-*n*-heptyloxybenzoyloxy) toluene.

System Ib:

Component *A*: 4-Nitrobenzylidene-4′-*n*-heptyloxyaniline.
Component *B*: 4-Nitrobenzylidene-4′-*n*-octyloxyaniline.

In this system both the components are the members of the same homologous series having strongly polar terminal —NO_2 group. The binary phase diagram is obtained by plotting mole percent concentration of the component *A* versus transition temperatures (Figure 2).

Ideal phase diagram is obtained. Smectic–nematic as well as nematic–isotropic transition temperature curve are linear in nature.

Binary Systems Type II: Polymesogen + Non-mesogen:

System IIa:

Component *A*: 4-Nitrobenzylidene-4′-*n*-heptyloxy aniline
Component *B*: 4-Methoxy benzylidene-4′-toluidine

Component *B* is a non-mesogen. Reference to (Figure 3) shows the non-linear behaviour for nematic–isotropic transition temperature

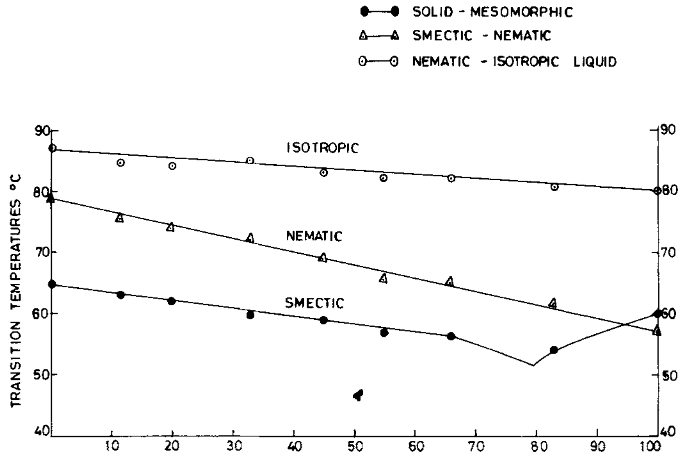

FIGURE 2 System Ib: mole % of 4-nitrobenzylidene-4′-*n*-heptyloxyaniline. 4-Nitrobenzylidene-4′-*n*-heptyloxyaniline: 4-nitrobenzylidene-4′-*n*-octyloxyaniline.

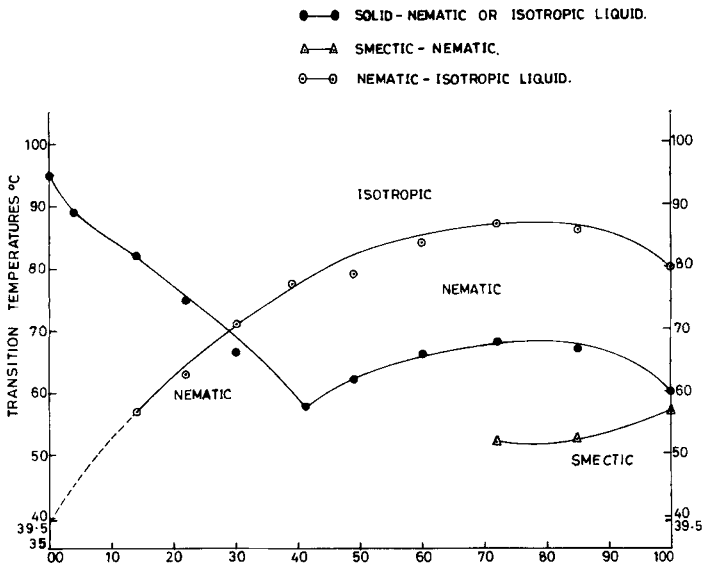

FIGURE 3 System IIa: mole % of 4-nitrobenzylidene-4′-*n*-heptyloxyaniline. 4-Nitrobenzylidene-4′-*n*-heptyloxyaniline: 4-methoxybenzylidene-4′-toluidine.

curve and the maxima is observed at 72 mole percent concentration of component *A*. N–I transition temperature curve falls off after exhibiting maxima and the monotropic nematic mesophase is observed upto 14 mole percent concentration of component *A*, beyond this the system becomes non-mesogenic. N–I transition temperature curve is extrapolated to obtain latent transition temperature for the component *B*. The extrapolated value for the latent transition temperature for component *B* (4-Methoxy benzylidene-4′-toluidine) is *39.5 °C* (Figure 3). Lohar and Shah[15] have obtained extrapolated latent transition temperature for the same compound in two different systems which is 39.0 °C. The value of latent transition temperature is almost the same in both the studies. The nematic–smectic transition temperature curve also exhibits little deviation from linearity and after 66 mole percent concentration of component *A*, the smectic mesophase disappears and only nematic mesophase is observed.

System IIb:
Component *A*: 4-Nitrobenzylidene-4′-*n*-heptyloxyaniline.
Component *B*: 4-Nitrobenzylidene-4′-ethyl aniline

Component *B* is a non-mesogen. Both the components have strongly polar terminal—NO_2 group. The phase diagram is quite interesting (Figure 4), with even the small concentration of component *B*, the

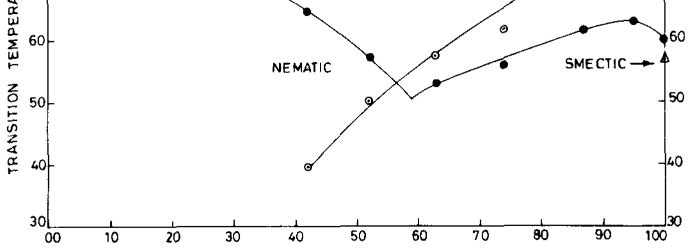

FIGURE 4 System IIb: mole % of 4-nitrobenzylidene-4′-*n*-heptyloxyaniline. 4-Nitrobenzylidene-4′-*n*-heptyloxyaniline: 4-nitrobenzylidene-4′-*n*-ethylaniline.

monotropic smectic phase of component *A* disappears. The N–I transition temperature curve shows the depressing tendency as the mole percent concentration of non-mesogenic component *B* is increasing and the nematic phase becomes monotropic and subsequently at higher concentration the mesophase disappears. The binary system does not exhibit non-linear behaviour as both components have strongly polar terminal —NO_2 group. This system is less mesogenic compared to series IIa.

Park *et al.*,[4] and Oh[6] and Griffin *et al.*[7,8] tried to explain non-linear behaviour of phase diagrams and induced smectic mesophases based on charge transfer complexes, lamellar structure and biaxial smectic A mesophases in binary systems where one of the component has strongly polar end group. However, Domon and Billard[9] have reported that it is not necessary that a mesogen should have a strongly polar terminal group. Lohar and Dave[16] also observed induced smectic phase as well as non-linear behaviour in their study of mixed mesogens.

Reference to Figure 1 indicates that induced smectic mesophase as well as non-linear behaviour is observed for smectic and nematic mesophases (System Ia). In the case of system IIa, even though second component is non-mesogenic, non-linear behaviour is observed for nematic–isotropic transition temperature curve. System Ib (Figure 2) exhibits linear behaviour for both the mesophases whereas in the case of system IIb linear behaviour is observed for nematic–isotropic transition temperature curve (Figure 4).

From the general observation that the compounds having strongly polar end group (—CN or —NO_2) exhibit bilayer smectic A mesophase, in absence of X-ray study we can safely presume that the smectic mesophase exhibited by component *A* would be a bilayer smectic A mesophase. If this is the case, then based on the models of Oh[6] and Griffin *et al.*[7,8] the linear and non-linear behaviour of the binary systems Ia to IIa for smectic–nematic transition temperature curve can easily be explained. However, the non-linear behaviour observed for the nematic–isotropic phase transition and the behaviour of systems IIa and IIb cannot be explained satisfactorily.

To consider the view of Park *et al.*[4] of charge transfer complexes in such binary systems the individual components as well as mixtures were subjected to UV and IR spectral screening. The spectral study does not suggest the formation of charge transfer complexes in solid state or in solution.

To account the non-linear behaviour of both mesophases as well as the observations of Dave *et al.*[1] and Schroeder *et al.*[2] and Domon and

Billard, modification of proposed models[6,7,8] is necessary. It seems that not only dipolar interactions but steric interactions also play its role in such binary systems. Few more binary systems are studied[17] in which components have similar structure as in the present study but possess additionally a lateral substituent. In such binary systems induced smectic mesophase is not observed.

Non-linear behaviour observed in number of binary systems definitely suggest that some sort of molecular complexation takes place and especially when smectic phase and/or nematic phases are enhanced, it indicates that such molecular complexes have higher thermal stabilities. This involves the energy considerations also.

Acknowledgments

Authors are thankful to the Faculty authorities and the Head of the Department for providing facilities. This work was supported by C.S.I.R., India.

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