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Phase diagram and optical anisotropy in binary mixtures of two mesogenic compounds

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Abstract : Binary mixtures of two mesogenic compounds are found to show very interesting induced smectic A, smectic C and cholesteric phases for different ranges of concentrations and temperatures. Optical anisotropy in the cholesteric phase is estimated Induced smectic phases observed in the mixtures of different concentrations show a variety of optical diffraction patterns and these have been investigated in detail Variation of pitch with concentration is also studied in the cholesteric phase Features like focal-conic and fan textures and optical diffraction effects are also illustrated.

Keywords : Phase transition, optical anisotropy, optical textures, optical diffraction and pitch

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1. Introduction

It is well known that the binary mixture of nematic and cholesteric compounds exhibit smectic and cholesteric phases over a large range of concentrations and temperatures [1,2]. Mixtures with very low percentages of a cholesteric in a nematic compound exhibit a finger print pattern and are found to have a large pitch value [3,4]. The concentration dependence of pitch is well established by earlier investigators using different techniques [4]. In the present investigation, we have used two liquid crystalline compounds, namely, cholesteryl-2-propyn-1-yl-carbonate (CPC) and N-ethoxybenzylidene-P-butylaniline (EBBA). In the present investigation we try to illustrate various optical diffraction patterns from smectic domains and also due to defects present in cholesteric phase in mixtures of CPC and EBBA.

2. Experimental

The samples used in this investigation were obtained from M/s Eastman Organic Chemicals, USA with a given minimum purity of 98%. The transition temperature (T_{N-I}) for EBBA is 78° C and (T_{C-I}) for CPC it is 95° C, which are determined using DSC and a Leitz polarising microscope in conjunction with a hot-stage. The transition temperatures of the samples are slightly less than the values reported in the literature. The density and refractive indices of CPC and EBBA were reported in our earlier paper [5]. Mixtures of about ten different concentrations were prepared. In the following, concentrations are defined as the weight percentage of CPC in the total weight of the mixture of CPC and EBBA. The phase transition temperatures of the mixtures were determined using DSC and polarising microscope and are shown in Figure 1. It is evident from the phase diagram that the concentrations between 1-9, 10-50 and 51-95 wt % of CPC in EBBA respectively correspond to cholesteric, smectic and

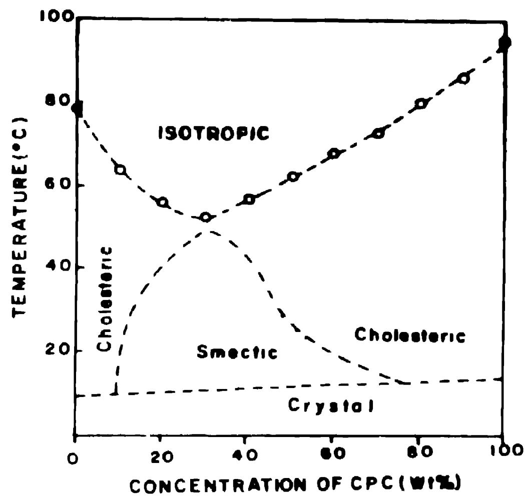


Figure 1. Phase diagram of mixture of CPC in EBBA

cholesteric liquid crystalline phases. The density (ρ) and refractive indices n_1 and n_2 ($n_1 > n_2$) in cholesteric phase for $\lambda = 5893$ Å for concentrations in the range 51 to 95% of CPC were determined as explained in our earlier paper [6]. The principal polarizabilities of the cholesteric phase in 51 to 95% of CPC at different temperatures were calculated using Lorenz-Lorentz relation using the measured values of density (ρ) and refractive indices n_1 and n_2 at different temperatures. For example for ordinary refractive index.

$$\left(n_1^2 - 1\right)/\left(n_1^2 + 2\right) = 4\pi/3N\alpha_{1\,\text{mix}}, \tag{1}$$

where

$$N = \left\{\left(x_1/M_1\right) + \left(x_2/M_2\right)\right\}\left(N_A\rho_{\text{mix}}\right). \tag{2}$$

M_1 and M_2 corresponds to the molecular weight of CPC and EBBA respectively. x_1 and x_2 corresponds to the weight fraction of CPC and EBBA respectively and N_A is the Avogadro number.

By using a similar equation for n_2 it is possible to calculate $(\alpha_2)_{mix}$ for the extraordinary ray.

The average polarizability $(\bar{\alpha})_{mix}$ can also be calculated using the formula

$$\bar{n}^2 - 1/\bar{n}^2 + 2 = 4\pi/3N\,(\alpha_{mix})_{expt}, \tag{3}$$

where

$$\bar{n}^2 = (2n_1^2 + n_2^2)/3.$$

The average polarizabilities of the concentrations between 51 to 95% of CPC at different temperatures have been calculated using the additivity relation

$$(\alpha_{mix})_{cal} = (N_1\alpha_1 + N_2\alpha_2)/(N_1 + N_2) \tag{4}$$

where N_1 and N_2 are the number of molecules per unit volume of CPC and EBBA respectively. α_1 and α_2 are the respective average polarizabilities. The variation of $\bar{\alpha}_{mix}$ (expt) and $\bar{\alpha}_{mix}$ (cal) with concentration CPC are shown in Figure 2.

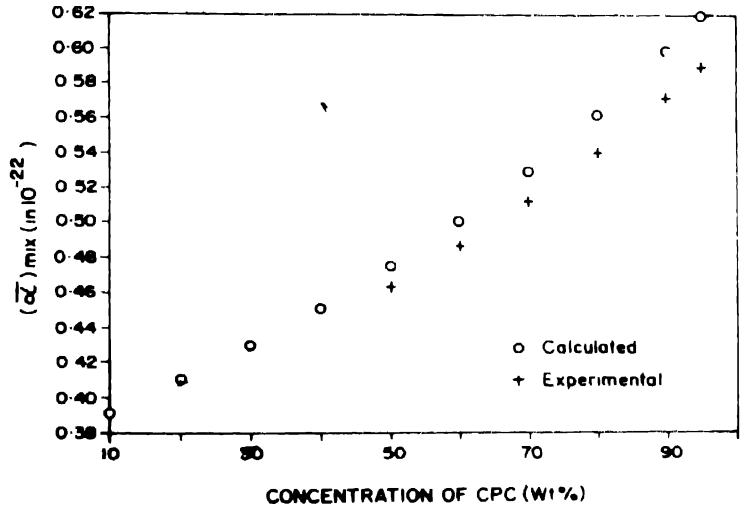


Figure 2. Mean polarizabilities $\bar{\alpha}_{mix}$ (in units of $10^{-22}\,cm^{-1}$) as a function of concentration of CPC in EBBA at 61° C.

It is pertinent to mention here that for the cholesteric phase, there are two refractive indices n_1 and n_2 for polarization perpendicular and parallel to the helical axis, where $n_1 > n_2$ [7]. Here n_2 will involve α_0, the polarizability transverse to the local nematic layer. However $n_1 = (n_e + n_0)/2$, where n_e and n_0 corresponds to the electric vector parallel and perpendicular to the local nematic director in the cholesteric layer respectively.

3. Results and discussion

The following conclusions emerge from our calculations. For a given concentration of the mixture in the range of 50 to 90% of CPC, the values of $(\alpha_1 - \alpha_2)$ exhibit a tendency for only a slight decrease with increase of temperature. From this, it is inferred that there is no major change in molecular ordering in the cholesteric phase with temperature. Further, with decreasing concentration of CPC the value of $(\alpha_1-\alpha_2)$ increases because the effective optical anisotropy associated with the molecule of EBBA is far greater than that associated with CPC. The mixtures of concentration from 10 to 50% of CPC exhibit the smectic phase. This is also supported by X-ray diffraction and optical textures studies. The values of $(\alpha_1-\alpha_2)_{mix}$ can also be compared with the values obtained from the additivity of the anisotropy of polarizability using the relation

$$(\Delta\alpha)_{mix} = (N_1\Delta\alpha_1 + N_2\Delta\alpha_2)/(N_1 + N_2), \tag{5}$$

$\Delta\alpha_1$ is $(\alpha_1 - \alpha_2)$ of CPC and $\Delta\alpha_2$ is $(\alpha_e - \alpha_o)/2$ of EBBA at corresponding temperature of the nematic phase. The factor half involved in the $\Delta\alpha_2$ arises because the molecules of EBBA are arranged in the layers of helical structure of the cholesteric phase. Eq. (5) can be written as

$$(\Delta\alpha)_{mix} - \Delta\alpha_2 N_2/(N_1 + N_2) = N_1\Delta\alpha_1/(N_1 + N_2). \tag{6}$$

The left hand side of the above equation is plotted against $N_1 / (N_1 + N_2)$ in Figure 3. The slope of the straight line is 6.13×10^{-24} cm^3 this being the value of $\Delta\alpha_1$ of CPC at the temperature of 68° C.

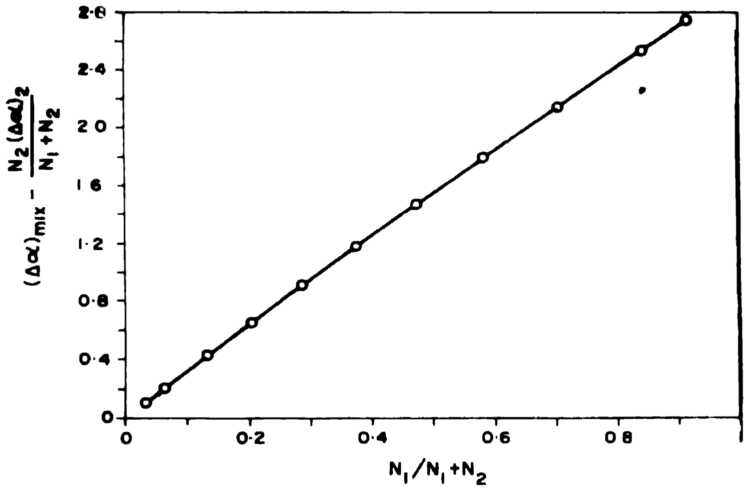


Figure 3. Variation of optical anisotropy with mole fraction. All calculations were made using equation 3 at 68° C. Here the value of $\Delta\alpha$ are in units of 10^{-24} cm^3.

Optical diffraction :

Earlier studies on binary mixtures reveals that when a small amount of a chiral substance is added to nematic liquid crystalline compounds, helical distortion results and a large pitch is introduced in the cholesteric phase [2]. For the observations of the optical textures the sample was sandwiched between a slide and a cover glass and was melted by keeping it in a hot-

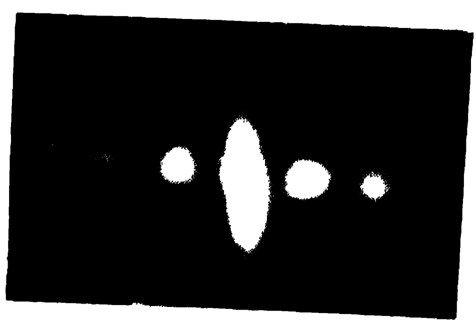
Plate I

(a)

(b)

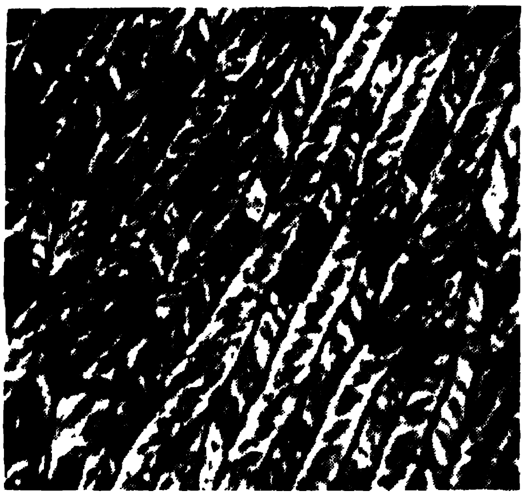
Figure 4(a,b). Microphotographs of focal conic texture of smectic A phase with 25% of CPC in EBBA

(a)



(b)

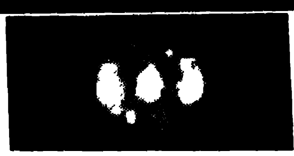
Figure 5 Microphotographs of 25% of CPC in EBBA. (a) Typical interlocking structure. (b) Optical diffraction patterns obtained from the interlocking structure.



(a)

Figure 6 Microphotographs of 35% of CPC in EBBA. (a) Leaflet domains.

(b)



(b′)

Figure 6 Microphotographs of 35% of CPC in EBBA. (b) Optical diffraction patterns obtained from the leaflet domains (b′) Lower magnification of (b).

(*a*) (*b*)

Figure 8. Microphotographs of 15% of CPC in EBBA. (a) Sanded domain texture. (b) Vertical optical diffraction patterns obtained with the above texture.

Figure 9. Microphotograph of broken-focal conic texture with 40% of CPC in EBBA.

stage. The optical textures observed in the range of concentrations 1 to 10% of CPC are finger print pattern with large values of pitch. It is also confirmed that there is a periodic variation of refractive index for the light polarized along the direction of the stripes. When the light is made to fall in a direction parallel to the cholesteric layer, the usual circular optical diffraction is observed [7]. Recently, Suresh *et al* (1992) have studied the optical diffraction in cholesteric and chiral smectics with reference to the polarization aspects of the patterns using Raman-Nath theory [8].

The samples with concentration range from 10 to 50% of CPC exhibit focal-conic fan shaped textures which are characteristic of smectic A phase (see Figures 4 (a,b)). The smectic A phase appears to be unstable and changes over to the smectic B phase which exhibits characteristic mosaic texture before passing over to crystalline phase. In the concentration range between 25 to 40% of CPC, before the smectic A phase pass over to smectic B phase, the focal-conic texture transforms to broken focal-conic which is characteristic of smectic C phase. The specimen with 25% of CPC exhibits smectic A phase at high temperature and slowly undergoes a transformation to interlocking structure at room temperature. The typical banded structure displays an optical diffraction pattern of several orders with a He–Ne laser beam, similar in nature to the patterns obtained from William domains in the nematic phase [9] and is shown in Figures 5 (a,b). The molecular ordering may be regarded as a periodic distortion of the layers in the smectic phase.

Mixtures with concentration of 35% of CPC also exhibit smectic A phase for a wide range of temperatures. This phase appears to be metastable and transforms to leaflet domains or chevron like texture at room temperature. Optical diffraction patterns obtained from this texture are shown in Figures 6 (a,b). Schematic representation of optical diffraction patterns is shown in Figure 7 and is similar to X-ray diffraction patterns observed for a well alligned

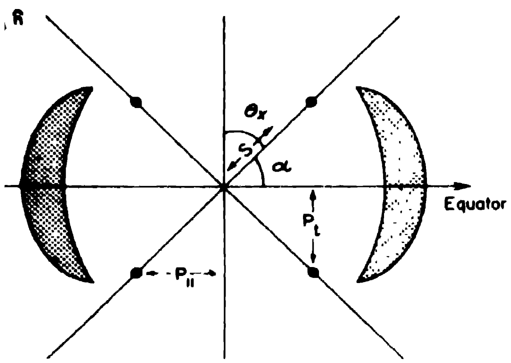


Figure 7. Schematic representation of diffraction pattern shown in Figure 6(b).

nematic sample [10]. Here, the centres of domains lie in a fairly well defined plane which makes an angle α with the direction of the director n in each domain. The dimension of the domain l has been estimated by using the relation $d/\sin\alpha = l$ [11] where d is the spacing evaluated by making use of the relation $2d \sin\theta = n\lambda$, $\lambda = 5893$ Å, $\theta = 1/2\tan^{-1}(S/D)$

where S is the distance between the symmetric inner spots and D is the specimen-film distance. The experiment was repeated for various values of D and for different specimens and in all the cases, the domain size is of the order of 6-7 microns. The samples with 15% and 20% of CPC also exhibit focal-conic shaped textures and finally they pass over to sanded domain structure. This texture displays a vertical optical diffraction pattern similar in nature to Aries pattern [12] observed with a specimen of randomly distributed uniform spherical particles but here the diffraction corresponds to particles which are rectangular in nature (see Figures 8 (a,b)). We would like to emphasize here that the sanded texture does not show any regular periodic arrangement of stripes or spots even when observed under high magnification. However the diffraction patterns obtained here appear to indicate regular periodic domains. If we pass on to the next concentration, 40% CPC also exhibits smectic A phase at higher temperature and then change over to broken focal-conic texture which is a characteristic of the smectic C phase at room temperature (see Figure 9). With this textures, V_v and H_v scattering patterns were obtained using the experimental method described by Krishnamurti *et al* (7). The V_v and the four leaf clover shaped H_v pattern confirm the fact that the principal direction of the refractive indices are parallel and transverse to the domains.

In the case of mixtures with 50% of CPC and above, the mesophase is characterised by a planar texture which corresponds to the cholesteric phase at high temperature. This mesophase is metastable and slowly transforms to smectic A phase at lower temperatures This smectic A phase again changes over to smectic E phase at room temperature.

The mixtures with low concentration of CPC in EBBA exhibit striped patterns characteristic of the cholesteric phase. The pitch of the cholesteric layers was measured using

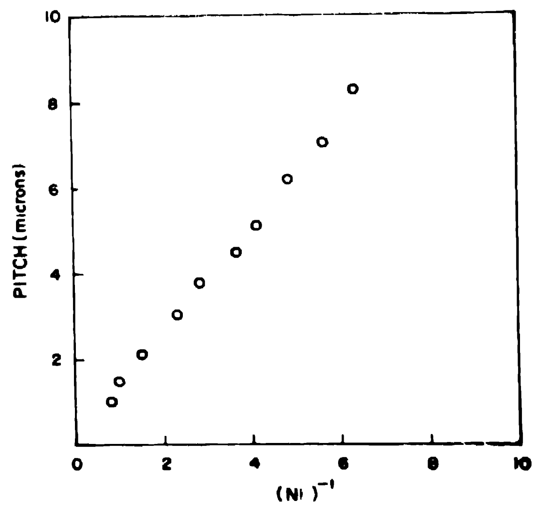


Figure 10. Variation of pitch of the cholesteric phase in the mixture of concentration of 10% of CPC. Here N_1 represents the number of molecules of CPC per unit volume of the mixture. The values of N_1 are in units of 10^{-19}/cc.

optical diffraction of striped pattern observed between crossed polars for concentrations between 1 to 10 wt% of CPC. The variation of pitch with concentration is shown in Figure 10.

4. Conclusions

The above study, apart from revealing numerous beautiful textures associated with the various cases, has enabled us to reach the following conclusions.

i) For mixtures with concentrations of CPC 10% and above, the mesophase corresponds to smectic and it is evidenced by textures, X-ray diffraction pattern and optical properties.

ii) For concentrations with 10% of CPC and below the mesophase corresponds to cholesteric phase and typically characterised by striped pattern. We have also confirmed that the pitch of the helix is inversly proportional to concentration of the cholesteric compound.

iii) The mixtures of concentration 50% and above of CPC exhibit cholesteric phase as evidenced by optical properties and optical anisotropy measurements.

iv) The optical diffraction pattern obtained in various smectic phases indicates that there is systematic modification in molecular ordering in induced smectic phases of different concentrations. Finally, all the textures transforms to mosaic texture characteristic of the crystalline phase at room temperature.

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