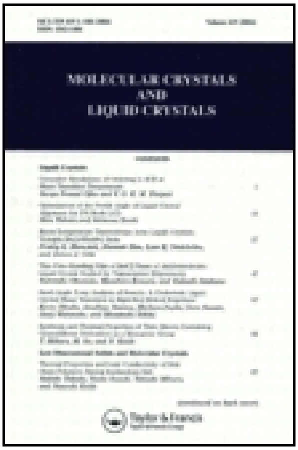

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Induced Chiral Smectic Phase in the Mixture of Cholesteric and Nematic Compounds

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The Mixture of cholesteryl benzoate (CB) and p-Ethoxy benzolidene-butylaniline (EBBA) exhibit, cholesteric and smectic phases. The sample of 20% concentration of CB shows I-S_A-S_{C*}-S_E-S_B phases while cooling from isotropic phase. Optical anisotropy of cholesteric phase has been estimated using refractive index data. X-ray, thermal and optical studies have been carried out for smecticA, chiral smectic and smecticE phases. In the case of S_{c*} phase the "d' spacing increases with increase of temperature. Pitch of the cholesteric phase and tilt angle of the S_{c*} phase have been estimated. Interesting optical textures of various concentrations have been illustrated in this investigation.

Keywords: Chiral Smectic; Pitch; Optical anisotopy

INTRODUCTION

The cholesteric phase is regarded as twisted nematic wherein the molecules are orientationally ordered, but at the same time they are rotationally disordered with respect to long axis[1-3]. It is well known that, if a small percentage of cholesteric liquid crystal is added to nematic, it results in the helical distortion and pitch of the phase increases. When the pitch is comparable to the wavelength of light, the phase becomes iridescent because of the selective reflection of the light. The recent studies on the mixture of cholesteric and nematic liquid crystals reveals that the mixture exhibits frustrated blue phase, twisted grain boundary phase, tilted phase, cholesteric phase and quasi-crystalline phase[4-6]. Because of the tremendous potentialities of the liquid crystals in the field of display device technology, we have proposed the studies on the optical and thermal properties of mixture of cholesteric and nematic liquid crystals. Optical, thermal and X-ray studies have been carried out to understand the intermolecular interactions and the nature of the induced smectic phases exhibited by the mixtures.

Experiment

The liquid crystalline compounds viz cholesteryl benzoate (CB) and p-Ethoxy benzolidene-butylaniline (EBBA) used in this investigation are obtained from M/s. Eastman organic chemicals and Automergic chemicals, USA. The chemicals are purified twice with benzene and transition temperatures are determined using DSC and polarizing microscope. The mixtures of about twenty different concentrations were prepared and are defined as the weight percentage of CB in the total weight of the mixture of CB and EBBA. The phase transition temperatures of induced phases of the mixtures were determined using polarizing microscope and DSC. The phase transition temperatures are drawn against concentration as shown in Fig.1.

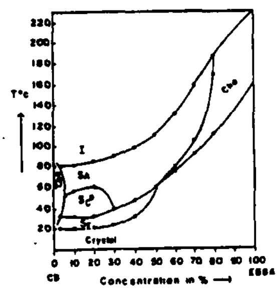

FIGURE 1 Phase diagram of mixture of CB in EBBA

The phase diagram shown in Fig.1 illustrates that the mixtures of concentration upto 6% of CB in EBBA exhibit a cholesteric phase and the intermediate concentrations from 7 to 30% of CB exhibits an induced smectic phase. For example when the concentration of 20% of CB cools from isotropic melt shows I-S_A-S_{C*}-S_E-Cr phases sequentially. The DSC traces for some samples are obtained from Raman Research Institute, Bangalore. The change in the entropy and enthalpies are also calculated. The concentration from 30 to 80% of CB exhibits only smecticA phase in large temperature range where as the mixture with 80% of CB and above exhibit only cholesteric phase.

Results and Discussion

Optical Anisotropy

In order to estimate the optical anisotropy of the mixtures exhibiting cholesteric phase from 1 to 6% of CB are considered. The density and refractive indices n_1 and n_2 ($n_1 > n_2$) at different temperatures are measured using Abbe refractometer and precision goniometer spectrometer. The density of the mixture is measured using the method as explained in our earlier paper[3]. The refractive index and the density data are given in table 1.

TABLE 1 Measured values of densities, refractive indices and calculated values of polarizabilities

(Tc-T)°C	ρ_{mix}	n_1	n_2	α_1	α_2
2	0.9814	1.571	1.547	33.6954	35.1192
4	0.9845	1.573	1.548	33.5891	35.0083
6	0.9866	1.575	1.550	33.5184	34.9346
8	0.9887	1.576	1.553	33.4464	34.8596
10	0.9917	1.578	1.555	33.3453	34.7542
12	0.9938	1.579	1.558	33.2748	34.6808
14	0.9959	1.581	1.559	33.2046	34.6076
16	0.9990	1.584	1.561	33.1016	34.5003
18	1.0012	1.586	1.563	33.0289	34.4244
20	1.0033	1.589	1.568	32.9597	34.3524

Heare n_1 and n_2 are the refractive indices of the ordinary and extraordinary rays respectively. In the case of 20% of CB it is very interesting to note that there is a jump in the value of the refractive indices at phase transition. The refractive index of CB is measured using precision goniometer spectrometer. The index data of EBBA used in our calculation are from our earlier studies[7]. The respective mean polarizabilities α_e and α_o of EBBA and α_1 and α_2 of CB could be obtained using Neugebauer relation[8]. In the case of mixtures the refractive indices should satisfy the equation,

$$\frac{\bar{n}^2-1}{\bar{n}^2+2} = \frac{4\pi}{3}\left[N_a\alpha_a + N_b\alpha_b\right]$$

$$= \frac{4\pi}{3} N\bar{\alpha}_{mix} \qquad (1)$$

Where N_a and N_b are the number of molecules of CB and EBBA respectively in unit volume of the mixture.

$$\bar{n}^2 = \frac{2n_1^2 + n_2^2}{3}$$

$$\therefore N_a = \frac{x_a}{x_a + x_b}\left(\frac{N_A}{M_a}\right)\rho_{mix} \qquad (2)$$

Where X_a and X_b are the weight fraction of CB and EBBA respectively. N_A is the avagadro number. M_a is molecular weight of CB.

$$N = N_a + N_b$$

similarly,

$$N_b = \frac{x_b}{x_a + x_b}\left(\frac{N_A}{M_b}\right)\rho_{mix} \qquad (3)$$

M_b is the molecular weight of EBBA

Therefore

$$N_{mix} = \left(\frac{x_a}{M_a} + \frac{x_b}{M_b}\right)\left(\frac{N_a}{x_a + x_b}\right)\rho_{mix} \qquad (4)$$

The values of α_l and α_2 in the cholesteric phase of the mixtures are calculated using refractive index and density data. The calculated values may be compared with that to be expected from additivity of the anisotropy of polarizabilities as expressed by the following relation.

$$(\Delta\alpha)_{mix} = (\alpha_1 - \alpha_2) = \frac{N_a(\Delta\alpha_a) + N_b(\Delta\alpha_b)}{N_a + N_b} \qquad (5)$$

Where $\Delta\alpha_b$ is equal to $(\alpha_e-\alpha_o)/2$ of EBBA at corresponding temperatures in the the nematic phase and $\Delta\alpha_a$ is equal to $(\alpha_1-\alpha_2)$ of CB. The factor half involved in the expression for $\Delta\alpha_b$ arises because the molecules of EBBA are arranged in the layers of the helicoidal structure of the cholesteric mesophase. From equation (5), it follows that

$$(\Delta\alpha)_{mix} - \frac{N_b\,(\Delta\alpha_b)}{N_a + N_b} = \frac{N_a\,(\Delta\alpha_a)}{N_a + N_b} \qquad (6)$$

Hence a graph of the left hand side of the above equation against N_a/N_a+N_b should be linear and this is actually the case in Fig.2. The slope of the graph is equal to $(1.4182 \times 10^{-24} cm^3)$, this being the value of $(\Delta\alpha_a)$ of CB at $(T_c-T) = 6°$ C.

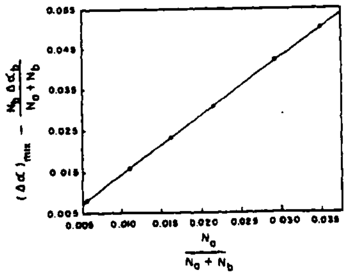

FIGURE 2 Variation of optical anisotropy with mole fraction. Here the value of $\Delta\alpha$ are in units of 10^{-24} cm^3.

Optical Textures

When a cholesteric compound is added as impurity to a nematic compound the pitch of the cholesteric phase increases in dilute limit of the mixtures. Indeed, if the pitch is sufficiently large it is possible to observe stripes under the polarizing microscope. The stripes associated with the helicoidal structure, clearly indicates that the mesophase is cholesteric. The concentrations up to 6% of CB exhibits striped pattern when they are cooled from isotropic to room temperature which corresponds to cholesteric phase. Microscopic twisting power β of the solute in the mixture 1-6% of CB is calculated,

$$\frac{2\pi}{P} = 4\pi\beta C$$

Where P is the pitch of the helix and C is the concentration of CB

$$\therefore \ \beta = \frac{1}{2PC}$$

The pitch of the cholesteric phase against concentration is drawn and shown in Fig.3.

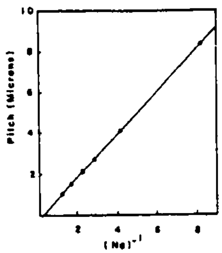

FIGURE 3 Variation of pitch of cholesteric phase with $(Na)^{-1}$. Here Na represents the number of molecules of CB per unit volume of the mixture and the values of Na are in units of 10^{-19}/cc

The Fig.3 confirms that at low concentration pitch is inversely proportional to concentration of the cholesteric compound. The mixture of concentration from 7 to 30% of CB exhibits a polymorphism in smectic mesophase. When the specimen is cooled from isotropic melt the genesis of the nucleation points grow with batonnets which are characteristic of smectic mesophase and these batonnets transform into focal conic texture on further cooling.

It is observed from the investigation that mixtures with intermediate concentration exhibit induced chiral smectic phase. In the case of mixture with 20% of CB the phase changes from I-S_A-S_{c*}-S_E-S_B sequentially when it cools from isotropic phase. The focal conic texture shown in fig.4 is the characteristic of S_A phase.

This phase is metastable and change over to S_{c*} phase exhibiting radial fringes on the fans of the focal conic textures which is characteristic of chiral smectic phase and shown in Fig.5.

The twist can be of the constituent molecules of the phase of chiral they possess point symmetry in the relation to their asymmetric centers. When they packed in the layers where the molecular long axes are tilted with respect to the layer planes and the phase has C_2 space symmetry[8]. The stacking of the layers one on top of the other results in the tilt precessing about the normal to the layers creating a macroscopic helical structure.

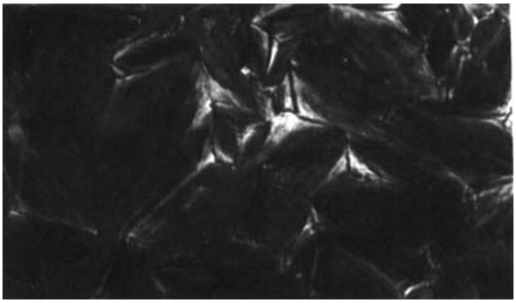

FIGURE 4 Microphotograph of S_A phase with 20% of CB in EBBA (See Color Plate XV at the back of this issue)

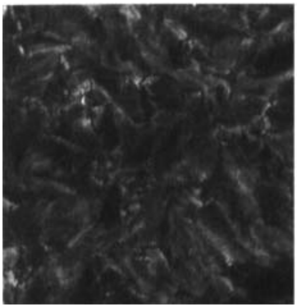

FIGURE 5 Microphotograph of S_{C*} phase with 20% of CB in EBBA (See Color Plate XVI at the back of this issue)

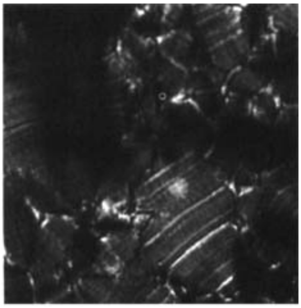

FIGURE 6 Microphotograph of S_E phase with 20% of CB in EBBA (See Color Plate XVII at the back of this issue)

The chiral smectic phase is also metastable and changes over to smecticE phase on cooling. The fans are crossed by a number of arcs which is characteristic of the smecticE phase which is shown in fig.6. The optical textures and X-ray diffraction studies confirm the herringbone structure of the smecticE phase. In smecticE phase the molecules are arranged in zig zag conformation in successive layers[9,10]. Finally the specimen crystallizes with smecticB phase.

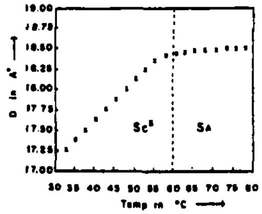

FIGURE 7 Variation of layer spacing with temperature.

To understand the variation of the layer spacings in SmecticA and Chiral Smectic phases X-ray diffractometer traces were taken. The traces were obtained for the mixture of 20% of CB at different temperatures. It is observed that as temperature increases the layer spacing also increases in S_{c^*} phase but in SmecticA phase the layer spacings are almost constant. The variation is shown in Fig.7. The tilt angle of the molecule in S_{c^*} phase is calculated using 'd' values obtained from X-ray studies.[11]

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