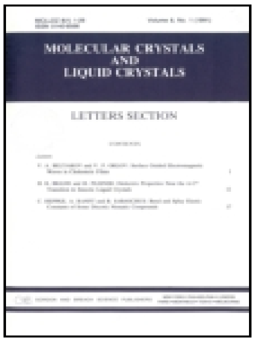

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Study on Optical Characterization of Binary Mixture of Two Thermotropic Liquid Crystals

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In the present work, our investigation is to study the optical and thermal properties of the binary mixture of cholesteric and nematic compounds, namely, cholesteryl oleate (CO) and p-Methoxybenzylidene-p-Ethylaniline (MBEA), which exhibits a very interesting liquid crystalline cholesteric and induced smectic phases like SmA, SmC, SmC, and SmE phases sequentially when the specimen cooled from isotropic phase. The temperature variation of optical anisotropy is also discussed. X-ray studies have been carried out to understand the intermolecular interactions in the mixture. With the help of phase diagram, the phase behavior has also been discussed.*

Keywords Binary mixture; induced chiral smectic phases; mesomorphism; optical anisotropy; phase transition; pitch

Introduction

Liquid crystal technology had a major effect in many areas of science and technology [1,2]. The most common application of liquid crystal technology is a liquid crystal display, which has grown to a multi-billion companies. From simple wrist watch, to an advanced computer screen liquid crystalline displays have evolved into a versatile interface. Liquid crystalline display uses much less power than that cathode ray tubes use. For many application of liquid crystal characteristics need to be satisfied such as stability of mesophase range and existence of phases at a desired temperature. Liquid crystal materials generally have several common characteristics; one of the characteristics is the transition temperature which is measured over temperature range of phases. To achieve useful temperature range, mixture can be used. The anisotropy of the physical properties is very important not only from the viewpoint of molecular theory but also practical applications, because it strongly affects the electro-optical properties of liquid crystal display. Recently, liquid crystal mixtures are used to enhance physical properties of these materials. Small concentrations of optically active material are mixed with emetic compounds shows changes in their behavior. Progress in understanding liquid crystalline phases also helps the understanding of more complex soft materials such as cell membrane and of natural processes—e.g., certain diseases such as sickle-cell anemia.

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In the present investigation, our aim is to carry out the study of optical and thermal properties of the binary mixture of cholesteric and nematic liquid crystalline compounds. All concentrations of the given mixture exhibit Iso→Ch→SmA→SmC→SmE→Cryst phases sequentially when they are cooled from isotropic phase. Optical and X-ray studies have been carried out to understand the intermolecular interactions in the mixture.

Experimental Studies

In the present investigation, we have studied binary mixtures of liquid crystals, namely, cholesteryl oleate (CO) and *p*-Methoxybenzylidene-*p*-Ethylaniline (MBEA), which are obtained from M/s Eastmann Organic Chemicals, USA. The chemicals are purified twice with benzene. Mixtures of 20 different concentrations of CO in MBEA were prepared. The phase transition temperatures of the mixtures were determined using Leitz-polarizing microscope in conjunction with hot stage. Refractive indices n_1 and n_2 for 5893 Å in cholesteric phase of the mixture were measured using Abbe refractometer and also Goniometer spectrometer at different temperatures [3]. Differential scanning calorimetry thermograms were taken for mixture of some concentrations using the Perkin-Elmer DSC II Instrument facility available at Raman Research Institute, Bangalore, India. The X-ray diffraction studies were undertaken by using JEOL-X-ray diffractometer. The density and refractive indices of the mixtures were measured at different temperatures employing the technique described in our earlier paper [4]. Electrical conductivity measurements of the given mixture at different temperatures were carried out using digital LCR meter and a proportional temperature control unit.

Theoretical Analysis

General Theory on Polarizability

The electric displacement $\vec{D}$, field intensity $\vec{E}$, and electric polarization $\vec{P}$ are related by

$$\vec{D} + \in_0 \vec{E} + \vec{P}$$

Since

$$\vec{D} = \frac{q}{A} = \frac{\in_0 \in_r q}{A \in_0 \in_r} = \in_0 \in_r \vec{E} = \in \vec{E}$$

Where

$$\in = \in_0 \in_r$$

Therefore,

$$\in \vec{E} = \in_0 \vec{E} + \vec{P}$$

$$\vec{P} = \in_0 \in_r \vec{E} - \in_0 \vec{E} = \in_0 \vec{E}(\in_r - 1)$$

$$(\in_r - 1) = \frac{\vec{P}}{\in_0 \vec{E}}$$

Where $\in_r$ is the electrical susceptibility of the liquid crystalline medium.

When electric field is applied, the dipole length increases and the dipole moment is given by

$$\overrightarrow{\mu_e}\vec{E}$$

$$\overrightarrow{\mu_e} = \alpha_e \vec{E}$$

Where α_e is called electronic Polarizability.

The dipole moment for unit volume called electronic polarization is given by

$$\vec{P}_e = N\overrightarrow{\mu_e} = N\alpha_e \vec{E}$$

Where N is the number density of molecules of liquid crystal.

But

$$\vec{P}_e = \in_0 \vec{E}(\in_r - 1)$$

Therefore

$$\in_0 \vec{E}(\in_r - 1) = N\alpha_e \vec{E}$$

or

$$(\in_r - 1) = \frac{N\alpha_e}{\in_0}$$

Polarizing Microscopic Studies

Polarizing microscope is the most widely used method in identifying different phases. Liquid crystal substances placed between two glass cover slips. Depending on the boundary condition and the type of phase, various textures which are characteristics of a phase are observed. Usually, the textures changes while going from one phase to another. Polarizing microscopy is powerful tool when used in combination with miscibility of binary mixtures. Liquid crystals phases possess characteristic textures when viewed under polarized light. These textures, which can often be used to identify phases, result from defects in the liquid crystals. Polarizing microscopy is used for various phases like nematic, cholesteric, and induced smectic phases such as SmA, SmB, SmC*, SmC, SmE etc. The liquid crystalline material goes from solid to liquid crystalline phase, the degree of length order decreases. This is expressed by a decrease in order parameters. In case of orientational disorder, it is possible to see changes between different liquid crystal phases during the heating and cooling cycles of liquid crystals.

Phase Diagram

The partial phase diagram as shown in Fig. 1, which is drawn by considering the phase transition temperatures against the concentrations of the given mixture, clearly illustrates the presence of CO in MBEA. Here, partial phase diagram shows a very interesting cholesteric, smectic-A, smectic-C*, smectic-C, and smectic-E phases, respectively, at different temperatures. The phase diagram clearly indicates that the mesomorphism of the mixture is

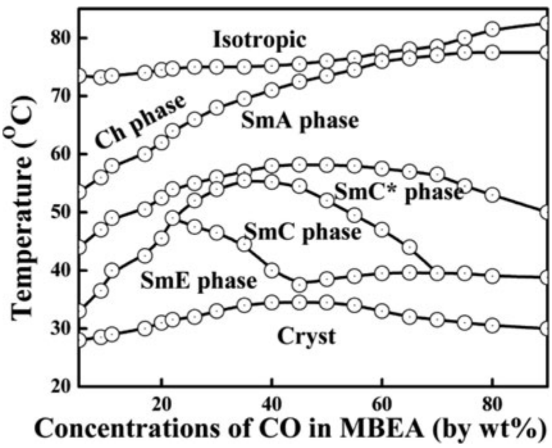

Figure 1. Partial phase diagram for the mixture of CO in MBEA.

thermodynamically stable for all concentrations of CO in MBEA. In our experimental studies, the different liquid crystalline phases have been identified on the basis of microscopic texture.

Optical Texture Studies

For the purpose of optical texture studies, the sample was sandwiched between a slide and a cover glass and then the optical textures were observed using a Leitz polarizing microscope in conjunction with a specially constructed hot stage. When mixtures with concentrations in the range of 5% to 15% of CO in MBEA molecules are slowly cooled from their isotropic melt, nucleation starts in the form of a small bubble and slowly grows radially and forms a fingerprint pattern, which is characteristic of the cholesteric phase with large values of pitch [5,6]. However, mixtures with concentrations from 20% to 40% of CO in MBEA exhibit a beautiful texture of cholesteric drops, as shown in Fig. 2(a). On further cooling, the cholesteric drops are slowly changed over to a well-defined focal conic fan-shaped texture, which is the characteristic of smectic-A phase and is shown in Fig. 2(b). The smectic-A phase is unstable and then changes over to the smectic-C* phase, which exhibits radial fringes on the fans of focal conic textures, which is characteristic of the chiral smectic-C* phase, as shown in Fig. 2(c). On further cooling, this phase changes over to the schlieren texture of smectic-C phase, as shown in Fig. 2(d) and then this phase change over smectic-E phase, which remains stable at room temperature.

Spiral Pitch and Helical Twisting Power

The cholesteric phase is regarded as twisted nematic phase, wherein the molecules are orientationally ordered, but at the same time they are rotationally disordered with respect to long axis [7]. It is well known that when a cholesteric compound is added as impurity to a nematic compound, the pitch of the cholesteric phase increases in dilute limit of the mixture, indeed, if the pitch is sufficiently large it is possible to observe stripes under the Leitz-polarizing microscope. When the pitch is comparable to the wavelength of light, the phase becomes iridescent because of the selective reflection of light. The stripes are associated with the helicoidal structures, which clearly indicate that the mesophase is

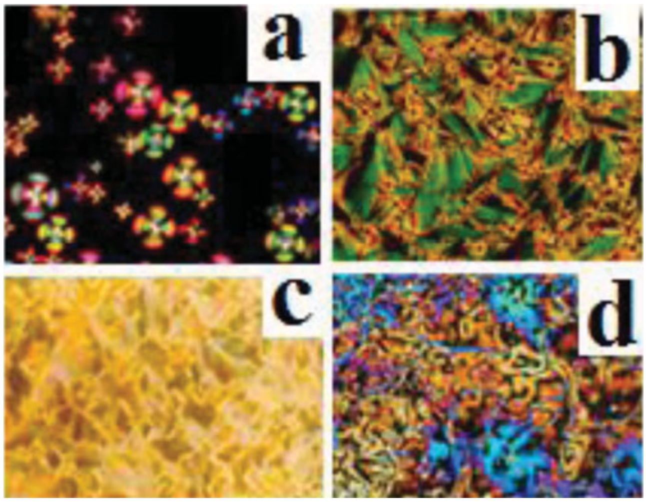

Figure 2. Microphotographs obtained in between the crossed polars, (a) Cholesteric drops phase (250X). (b) Focal conic fan-shaped texture of SmA phase (250×). (c) Chiral texture of SmC* phase (250×). (d) Schlieren texture of SmC phase (250×).

cholesteric. The mixtures with concentrations from 5% to 15% of the mixture exhibit a stripped pattern when they are cooled from isotropic phase at the respective temperatures, which corresponds to cholesteric phase. Microscopic twisting power β of the solute in the mixture 5% to 10% of CO is calculated using the formula:

$$4\pi\beta C = 2\pi/P$$

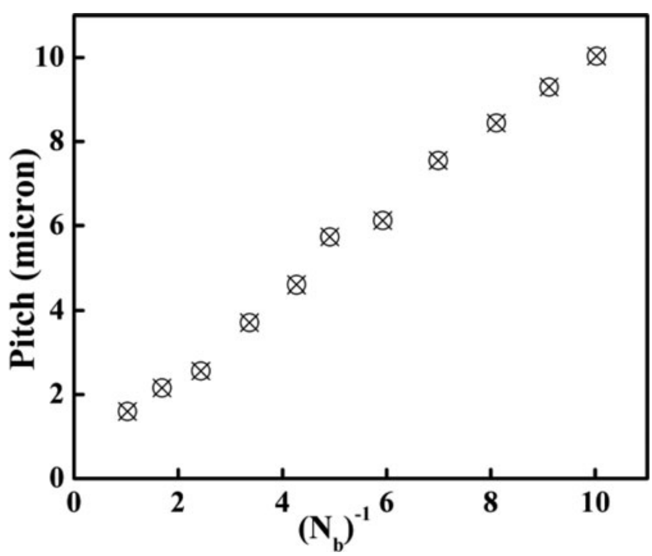

Figure 3. Variation of pitch of cholesteric phase with $(N_b)^{-1}$. Here N_b represents the number of molecules of MBEA per unit volume of the mixture. (units of N_b are 10^{+19}).

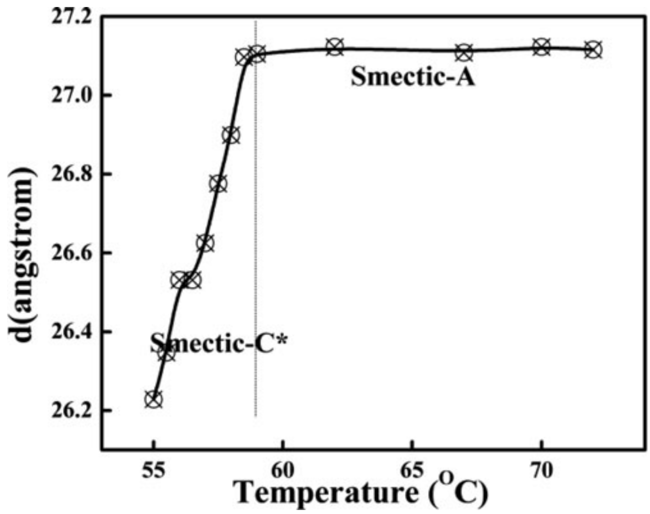

Figure 4. Variation of layer spacing with temperature for the sample of 30% CO in MBEA.

where P is the pitch of the helix and C is the concentration of CO

$$\beta = 1/2PC$$

The pitch of the cholesteric phase against concentration is drawn and shown in Fig. 3, which illustrates that at low concentrations of the cholesteric compound, the pitch is inversely proportional to the concentration of the cholesteric compound. The parameter β characterizes a helical twisting power value for the induced cholesteric phase. This result is in conformity with the rule that for a small concentration of cholesteric compounds in nematics.

X-Ray Studies

To understand the change in layer spacing's in smectic-A and smectic-C* phases with respect to temperature, X-ray diffractometer traces were taken. The traces obtained for the mixture of 30% CO in MBEA at different temperatures correspond to smectic-A and smectic-C* phases. It is observed that as the temperature increases the layer spacing also increases in smectic-C* phase. But in smectic-A phase, the layer spacing's are almost constant. These variations are shown in Fig. 4 [8,9].

Conclusions

The above studies apart from revealing a numerous textures and are associated with the various phases in the mixture have been enabled us to reach the following conclusions. The mixture with different concentrations from 5% to 90% of CO in MBEA exhibit cholesteric and induced chiral smectic phases depending on the temperatures. The drastic change in the value of density, refractive index, optical anisotropy of polarizabilities with the temperature unambiguously corresponds to smectic phases. The temperature variation of "*d*" spacing in smectic-C* phase has also been studied.

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