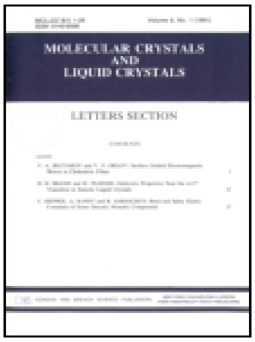

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Optical Studies on Smectic-Isotropic Phase Transition Behavior of Two Thermotropic Liquid Crystals

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ABSTRACT

The binary mixture of two compounds, viz., Cholesteryl laurate (CL) and diethyl 4, 4′-azoxy benzoate shows the cholesteric and smectic phases sequentially when the specimen is cooled from its isotropic phase. Refractive indices, birefringence, and optical transmittance have been measured by the optical technique. With the help of measured data, the macroscopic ordered parameter has been discussed. The temperature dependence of these parameters has also been discussed.

KEYWORDS

Binary mixture; molecular aggregation; optical anisotropy; optical transmittance; phase transition

Introduction

The importance of liquid crystal is increasing constantly due to their wide spread use in display technology and other devices [1, 2]. For the application of any liquid crystal, in practical device it must have suitable values of certain parameters like dielectric permittivity, dielectric loss, conductivity, refractive index, birefringence and viscosity, etc., with varying some conditions like temperature and electric field [3, 4]. Usually, it is very difficult to fulfill these conditions with a single liquid crystal sample. Hence liquid crystalline mixtures have come to play a very important role in display and device applications. Mesomorphic compound's melting point is depressed by addition of another substance and a mixed mesophase results, in which the liquid crystalline range may originate at a lower temperature. If physically added substance is structurally dissimilar to the original compound, only a small amount suffices to destroy liquid crystallinity because of its disrupting effect on the mesophase [5]. However, if it is structurally similar, liquid crystallinity may persist to high concentration of the second component and in fact over all compositions of both components are mesomorphic [6]. In order to achieve extended liquid crystalline temperature ranges, the binary/ternary, or multi-component systems offering the advantages of frequently exhibiting eutectic behavior in their crystal to mesophase transition while the mesophase to isotropic transition temperature varies almost linearly with composition [7, 8].

In the present investigation, we have been consider two compounds, namely, Cholesteryl laurate (CL) and diethyl 4, 4′-azoxy benzoate, which exhibits different liquid crystalline phases such as cholesteric, SmA, SmC, and SmB phases sequentially when they are cooled from isotropic phase. Experimentally measured data of refractive index and its anisotropy have

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been discussed. The macroscopic order parameters have been evaluated by the measured anisotropy of given mixture. Optical transmittance values have been measured with the variation of temperature to study the phase transition behavior.

Experimental section

The compound diethyl 4, 4′-azoxy benzoate used in this investigation was obtained from the Basic Pharma Life Science Pvt., Ltd., India, and it was further purified twice by a recrystallization method using benzene as a solvent. The CL was obtained from M/s East Mann Organic Chemicals, USA. Mixtures of 50% and 60% concentrations of CL and diethyl 4, 4′-azoxy benzoate were prepared and were mixed thoroughly. The mixture of given concentrations of CL and diethyl 4, 4′-azoxy benzoate were kept in desiccators for a long time. The samples were subjected to several cycles of heating, stirring, and centrifuging to ensure homogeneity. The phase transition temperatures of given concentrations were measured with the help of Leitz-polarizing microscope in conjunction with a hot stage. The samples were sandwiched between the slide and cover slip and were sealed for microscopic observations. Refractive indices values have been measured with the help of Abbe's refractometer (MITTAL 1245) whereas optical transmittance measurements have been done on polarizing microscope (CENSICO 7626). The constant temperature has been maintained by microprocessor based temperature controller Julabo F-25 (Germany) in all studies. The X-ray broadening peaks were obtained at different temperatures using JEOL diffractometer. Electrical-conductivity measurements of the mixture at different temperatures were carried out using digital LCR meter and a proportional temperature control unit [9].

Theoretical studies

The relationship between refractive index parallel (n_{II}) and perpendicular $n_\perp$ to the direction of molecular axis. The macroscopic order parameter can be obtained by modifying the equations [10] as

$$n_{II} = \bar{n} + \frac{2}{3} Q.\Delta n \tag{1}$$

$$n_\perp = \bar{n} - \frac{1}{3} Q.\Delta n \tag{2}$$

where $\bar{n}$ is the average refractive index and Δn is the birefringence corresponding to complete alignment $n_{II} = n_e$, $n_\perp = n_e$ [23,24]. From both the equations (1) and (2), we get

$$Q = \frac{n_{II} - n_\perp}{\Delta n} = \frac{n_e - n_o}{\Delta n} = \frac{\delta n}{\Delta n} \tag{3}$$

where $\delta n = n_e - n_o$

The value of macroscopic order parameter equal to 1 represents complete order at absolute temperature that is at 0 K $\delta n = \Delta n$. So the macroscopic order parameter (Q) has been obtained by extrapolating Δn for $T = 0$ K. This extrapolation is done on the linear portion of the graph drawn between birefringence Δn against ln (1-T/T_C) as evaluated by others [10, 11], here T_C is the smectic to isotropic phase transition temperature.

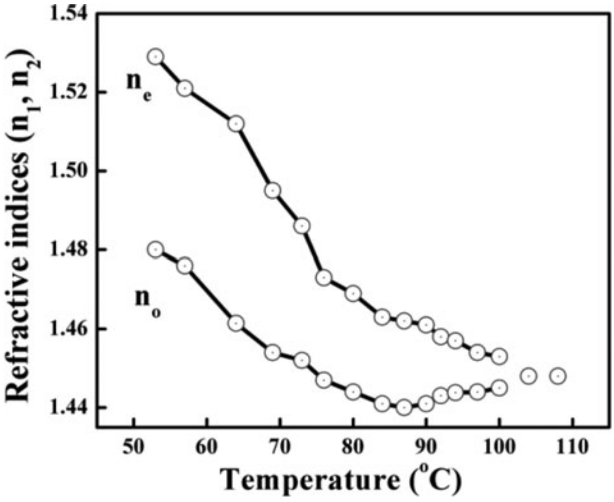

Figure 1. Temperature variations of refractive indices for the given sample.

Results and discussion

Optical texture studies

In the present study, optical textures exhibited by the samples were observed and recorded using Leitz polarizing microscope and constructed hot stage. The specimen was taken in the form of thin film and sandwiched between slide and cover glass. Concentrations of 50% and 60% binary mixture of CL and diethyl 4, 4′-azoxy benzoate have been considered for the experimental studies. Fifty percent and 60% of given mixture are slowly cooled from isotropic melt, the genesis of nucleation starts in the form of small bubbles and slowly grow radially, which form a spherulitic texture of cholesteric phase with large values of pitch [12, 13]. On further cooling the specimen, cholesteric phase slowly changes over to focal conic fan shaped texture, which is the characteristic of SmA phase. Further cooling the specimen, SmA phase changes over to schlieren texture of SmC phase. Before crystallizing the specimen, SmC phase slowly transform to SmB phase and then it becomes a crystalline phase.

Optical anisotropy

Temperature variations of refractive indices and optical birefringence studies for 50% concentrations of the given mixtures have been plotted in Figs. 1 and 2. From the figure, it can observe that the value of ordinary refractive index increases whereas the extraordinary refractive index decreases. Then the value of ordinary refractive index as well as extraordinary approaches sharply to isotropic refractive index and becomes same at smectic-isotropic transition after that the refractive index decreases almost linearly with the temperature like any liquid for given binary mixture. Optical birefringence value decreases slowly with increase in temperature and then its value decreases sharply with increase in temperature and becomes zero at smectic-isotropic transition for the mixture.

The temperature variation of macroscopic order parameter (Q) is presented in Fig. 3. The value of order parameter shows degree of orderness of the molecule. Therefore, the decrease in

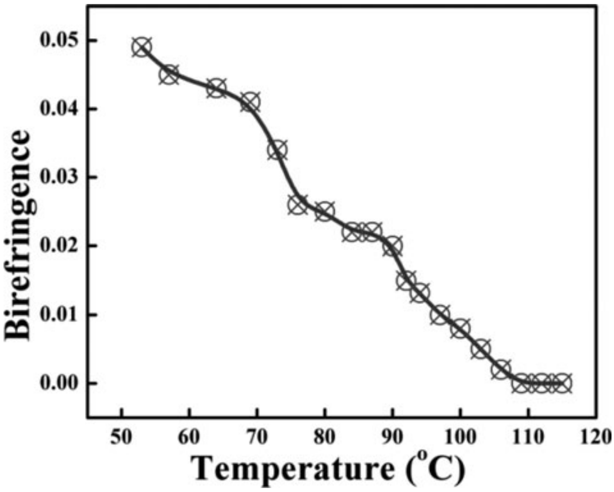

Figure 2. Temperature variations of optical birefringence for the given sample.

value of order parameter indicates the increase in randomness of molecules finally at smectic-isotropic transition. The order parameter value reaches to zero shows highest degree of randomness, i.e., the isotropic behavior of sample, but some of lyotropic materials shows the order parameter becomes high at all temperatures and at different concentrations [1].

Optical transmittance

The temperature variation of optical transmittance as shown in Fig. 4, which clearly illustrates that, the lower value of optical transmittance is almost constant in isotropic phase till 107°C, and then its value increases abruptly by lowering temperature and hence it indicates the isotropic-smectic phase transition. The higher value of optical transmittance is almost unaffected with decreasing temperature up to 45°C and after that its value decreases sharply which shows smectic-isotropic phase transition [14].

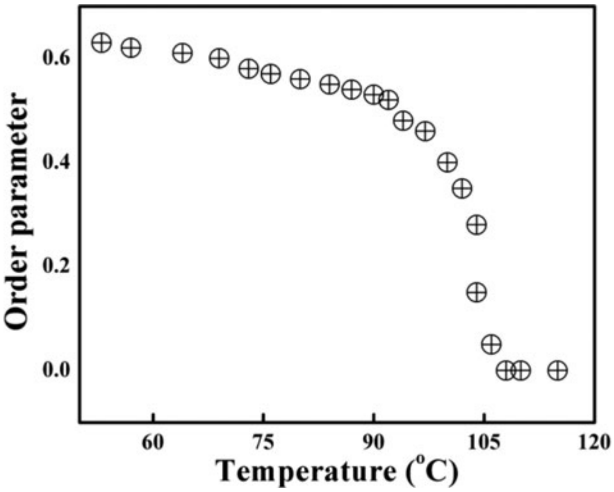

Figure 3. Temperature variation of macroscopic order parameter (*Q*) for the given sample.

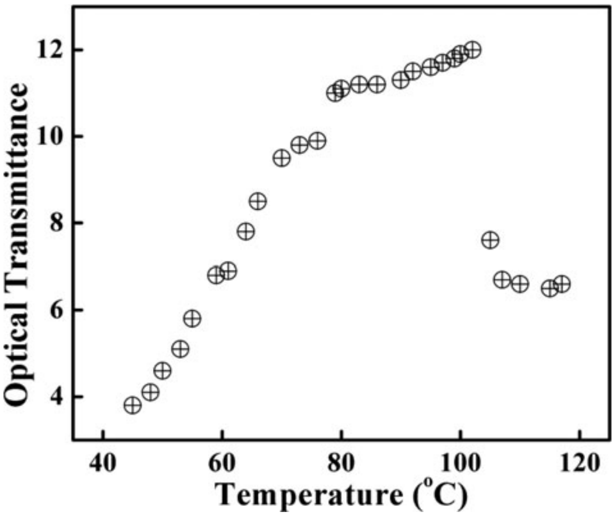

Figure 4. Temperature variation of optical transmittance for the given sample.

Conductivity measurements

Electrical-conductivity measurements are very helpful to study the smectic-isotropic phase transition with different temperature. An abrupt increase or decrease of electrical-conductivity with different temperature relates to the phase behavior of lyotropic, thermotropic, and also chromonic systems [15]. The temperature variations of electrical-conductivity in the present study are as shown in Fig. 5. The figure clearly illustrates that there is some increase in the value of electrical conductivity up to 57.5°C, while cooling from isotropic phase for the given binary mixture. With further decrease in temperature, the electrical conductivity starts decreasing as we move toward the room temperature. Decrease in the value of electrical conductivity is observed only after further cooling the specimen below 57.5°C. This suggests that, the grain size of molecular aggregates starts growing toward decreasing temperature and the system moves toward more orderliness. Finally, below 57.5°C

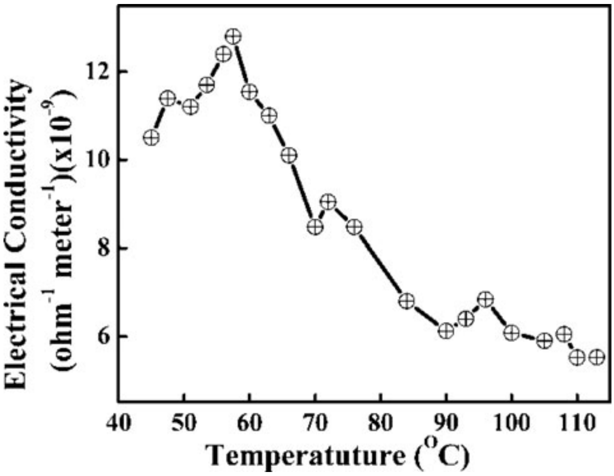

Figure 5. Temperature variations of electrical-conductivity σ ($\times 10^{-9}\ \Omega^{-1}\ \mathrm{m}^{-1}$) for the given sample.

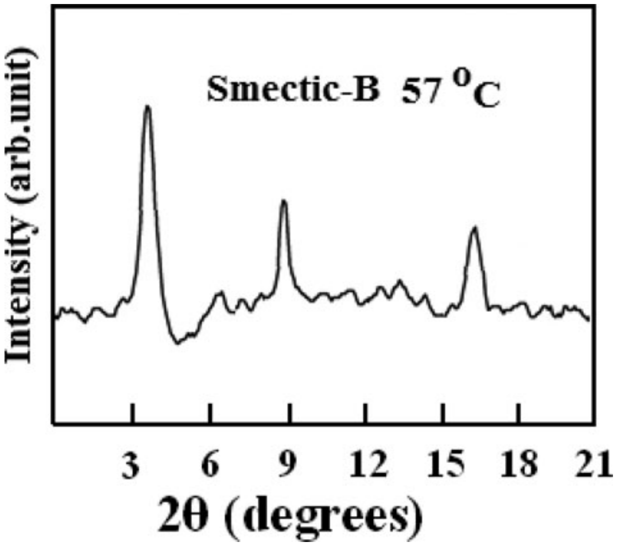

Figure 6. X-ray broadening spectrum for the given sample at 57°C temperature of SmB phase.

grains size of molecular aggregates becomes so large that the specimen starts moving toward crystalline nature [16, 17].

Characterization of nanoaggregation

The X-ray diffractometer traces obtained for the mixture of 50% of CL in diethyl 4, 4′-azoxy benzoate at temperatures 57°C is shown in Fig. 6, the diffraction peaks at these temperatures correspond to smectic-B phase respectively by using JEOL diffractometer with the settings: TC4, CPS400, channel width 100 for $\lambda = 1.934$ Å. X-ray diffraction study is an important method to determine the nanoaggregated grain size of the molecules for different liquid crystalline phases [18–20]. The deviation from perfect liquid crystallinity leads to broadening of the diffraction peaks. In order to estimate nanoaggregated grain size of the molecules for different liquid crystalline phases corresponding to broadening of X-ray diffraction peaks. We have used the Scherrer's formula

$$L = K\lambda/\beta\cos\theta,$$

where L is the crystalline size, λ is the wave length of X-ray radiation (1.934 Å), K is usually taken as 0.89, β is the line width at half maximum, and θ is the diffraction angle. Usually with decrease of temperature [21, 22], the nanoaggregated grain size of the molecules increases. From Fig. 6, broken banded focal conic fan texture smectic-B phase is energetically more stable, molecular ordering of this phase shows the intensity of three peaks. The nanoaggregated grain size of smectic-B phase are comes out to be 43.5318 nm. From the X-ray studies, we have been observed that, molecular ordering of the liquid crystalline phase increases with decreasing temperature. X-ray studies clearly illustrate that the nanoaggregated grain sizes are big enough to indicate that the molecular ordering [23] of layer structure increases as well as decrease the temperature.

Conclusions

The given binary mixture of two components shows the existence of cholesteric and smectic phases sequentially when the specimen is cooled from its isotropic phase. The measured and calculated values of refractive indices, birefringence, optical transmittance, and macroscopic ordered parameter are decreases sharply with increases in temperature and become zero at smectic-isotropic transition. The changes in value of electrical conductivity with temperature unambiguously correspond to phase transition between smectic and isotropic regions. Drastic changes in electrical conductivity are expected to be due to changes in the dimension of discs along with changes in the arrangement of molecular orientational order of the. Nano aggregated grain size of the molecules was found by X-ray diffraction technique.

Acknowledgments

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