

## **Opto-electrical and thermodynamic characterization of liquid crystalline materials**

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### **ABSTRACT**

We report the results of our studies on optical and thermal properties of binary mixture of compounds, viz., p-butoxybenzylidene, p-heptylaniline (BBHA) and cholesteryl nononate (CN). The mixture exhibits a very interesting twisted grain boundary (TGB) and re-entrant smectic-C (ReSmC) for different concentrations of BBHA sequentially when the specimen is cooled from its isotropic phase. The temperature variations of optical-density and electrical conductivity have been discussed. Thermodynamic studies have also been discussed to understand the phase stability, chemical structure and molecular dynamics of the binary mixture of liquid crystalline materials. © 2016 Trade Science Inc. - INDIA

### **KEYWORDS**

Binary mixture;  
Optical studies;  
Density;  
Electrical conductivity;  
Thermodynamic studies.

### **INTRODUCTION**

Liquid crystals are primarily liquids but also share properties of crystalline materials. Usually, liquids are characterized by isotropic macroscopic properties and by the ability to flow while crystals are characterized by long range positional order which leads to anisotropic macroscopic properties. Like liquids, liquid crystals exhibit fluidity. They are made up of organic molecules characterized by anisotropic molecular properties and by short range molecular interactions which couple over many molecular diameters to produce long range orientational order<sup>[1, 2]</sup>. These characteristics results are in anisotropic macroscopic properties such as birefringence, density, susceptibilities and optical studies etc.

In the present investigation, our aim is to carry out the study of different properties of binary mixture of liquid crystalline materials<sup>[3, 4]</sup>. Some of the concentrations of given mixtures exhibits a very in-

teresting twisted grain boundary (TGB) and re-entrant smectic-C (ReSmC) phases sequentially when they are cooled from its isotropic melt. Optical, thermodynamic and electrical conductivity have been discussed.

### **EXPERIMENTAL STUDIES**

The compound p-butoxybenzylidene, p-heptylaniline (BBHA) 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 cholesteryl nononate (CN) was obtained from M/s East Mann Organic Chemicals; USA. Mixtures of different concentrations of BBHA in CN were prepared and were mixed thoroughly. These mixtures of various concentrations of BBHA in CN 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 these 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. A capillary Pycnometer with a diameter of about 0.2 mm was used for density measurements. The permitted temperature control was  $\pm 0.1^\circ\text{C}$ . The level of liquid crystal in the capillary was read to  $\pm 0.01\text{mm}$  with a cathetometer. The absolute error in the density measurements was  $\Delta\rho = \pm 0.0001\text{ g/cc}$ . Electrical-conductivity measurements of the mixture at different temperatures were carried out using digital LCR meter and a proportional temperature control unit.

## RESULTS AND DISCUSSIONS

### Optical texture studies

The optical textures exhibited by the samples were observed and recorded using the Leitz polarizing microscope and specially constructed hot stage. The specimen was taken in the form of thin film and sandwiched between the slide and cover glass. The concentrations from 5% to 80% of binary mixture of BBHA in CN have been considered for the experimental studies. When the specimen of 45% BBHA in CN is cooled from its isotropic, it exhibits Iso-Cho-TGB-SmC-SmA-ReSmC-SmE phases sequentially. While the sample is cooled from its isotropic phase, nucleation starts in the form of minute bubbles and immediately the bubbles grow radially and form fingerprint pattern, which is characteristic of the cholesteric phase with large values of pitch<sup>[5, 6]</sup>. On further decreasing temperature of the sample, the cholesteric phase slowly changes over to smectic phase, passing through an intermediate phase and it is assigned by the appearance of mobile thread-like textures in the homeotropic region, which is the characteristic of twisted grain boundary (TGB) phase. The helical axes of twisted grain boundary (TGB) phase lies in a direction parallel to the smectic layer planes<sup>[7, 8]</sup>. On further cooling, thread-like TGB phase changes over to appearance of tilting the mol-

ecules are relative to smectic layers and then it is the characteristics of well defined schlieren textures of SmC. On further cooling the specimen, SmC phase may transform into the focal conic fan shaped texture of SmA phase. Microscopically observed transformation of SmC to SmA phase as shown in Figure 1. Molecular structural confirmations of SmA phase is stable at temperature  $60^\circ\text{C}$ : for thermal variations, the flexibility of molecular layers leads to distortions, which gives rise to optical patterns known as focal-conic textures. If there observed some different smectic phases: that differ from one another in a way of layer formation and they existing an order inside the molecular layers. In this system, the microscopic observations clearly indicate that: the given mixture with concentrations ranging from 35% to 60% of BBHA in CN exhibits a re-entrant SmC phase<sup>[9]</sup>. The lowest temperature mesophase of certain compounds exhibits two or more mesophases of the same type, over different temperature ranges. Re-entrant mesophases are most commonly observed when the molecules have strong longitudinal dipole moments. The sequences of re-entrant mesophases have also been found in binary mixtures of non-polar liquid crystalline compounds<sup>[10]</sup>. In the present system, some concentrations of BBHA at lower temperatures did not show the molecular aggregates in the preferred direction of alignment towards the crystalline phase, but it randomly oriented to form a re-

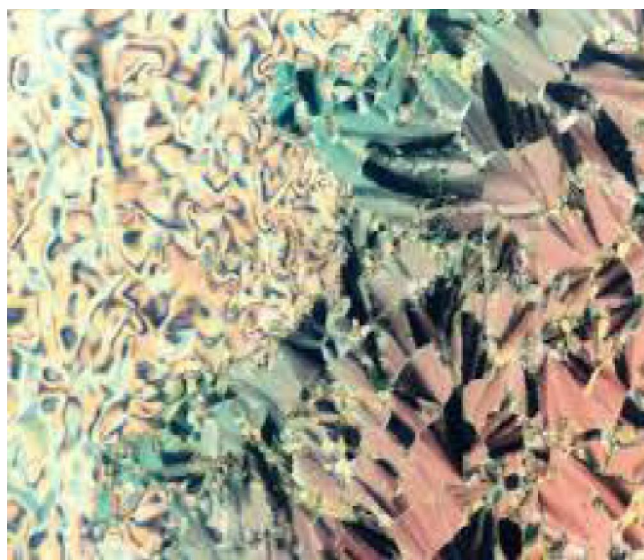
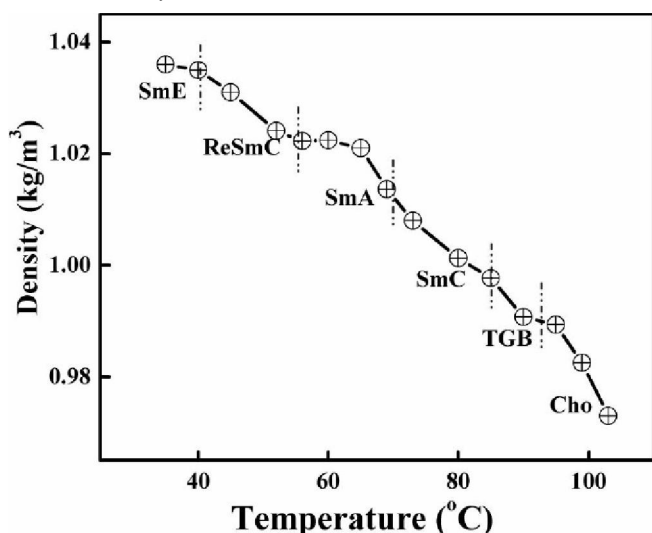


Figure 1 : Microscopically observed transformation of SmC to SmA phase

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**Figure 2 :** Temperature variations of density for the sample of 45% BBHA in CN

entrant SmC phase, and then this phase changes over to a focal conic fan-shaped herring bone pattern of the SmE phase and then it becomes crystalline phase, which remains stable at room temperature<sup>[11, 12]</sup>.

### Density measurement

Temperature variations of density for the sample of 45% BBHA in CN as shown in the Figure 2, which clearly illustrates that: the density increases linearly with decrease of temperature in the optical region between isotropic and crystalline phase of given mixture. The phase transition is very nearer to isotropic and cholesteric region, in this transition at particular region a sudden jump has been observed in the values of density. A sudden jump in the value of density shows the increases its value hence it indicates that: the phase transition region in between isotropic and cholesteric phase transition is probably first order. A sudden jump in the value of density at optical region is attributed to a sudden change in the molecular structure, that they were confirmed macroscopically by microscopic technique. The higher values of density in the cholesteric phase region are more than that of in isotropic region: which clearly indicates that, the tendency of increasing molecular order is more with decrease of temperature<sup>[13, 14]</sup>, the pre-transitional effects at optical region between isotropic and cholesteric phase transitions are found to observed on the lower side of the transition, which supported by Maier-Saupe

theory<sup>[15]</sup>. After isotropic transition, at cholesteric phase region the density of given mixtures increases linearly with decrease of temperature and then at the optical region between cholesteric and TGB phase transition: the values of density shows a increasing nature. From the measured of higher value of density of the given mixture and the literature survey of thermal expansion coefficient clearly indicate that: the transition is first order. The measured higher value of density and thermal expansion coefficient indicate that: the phase transition is first order. Our measurements are in accordance with Torza and Cladis on CBOOA. Densities of the given mixtures are increases gradually with decrease of temperature in TGB phase. The increasing values of densities: that has been experimentally observed at different optical regions with decrease of temperature towards the crystalline phase. The structural confirmations of molecular density of different liquid crystalline phases such as smectic-C-smectic-A- re-entrant smectic-C-smectic-E phases have been macroscopically observed by microscopic technique at different concentrations and at different temperature. The measurements of increasing values of densities across at different optical regions are more predominant than one to other optical regions.

### Conductivity measurements

Electrical-conductivity measurements are helps us to understand in getting better idea on the phase behavior with temperature. An abrupt increase or decrease of electrical-conductivity with temperature relates to the different liquid crystalline phase transition behavior of lyotropic and thermotropic systems<sup>[16]</sup>. The temperature variations of electrical-conductivity are shown in Figure 3. The changes were observed in electrical-conductivity, the values correspond to liquid crystalline phase transition of thermotropic and lyotropic systems respectively at different temperatures and they were also identified by DSC and optical texture studies. It was observed that, a change in electrical-conductivity at temperatures 93°C, 85°C, 70°C, 55°C, 40°C and 30°C respectively, which corresponds to phase transition from isotropic to Cho-TGB, TGB-SmC, SmC-SmA, SmA-ReSmC and ReSmC-SmE phases. This type

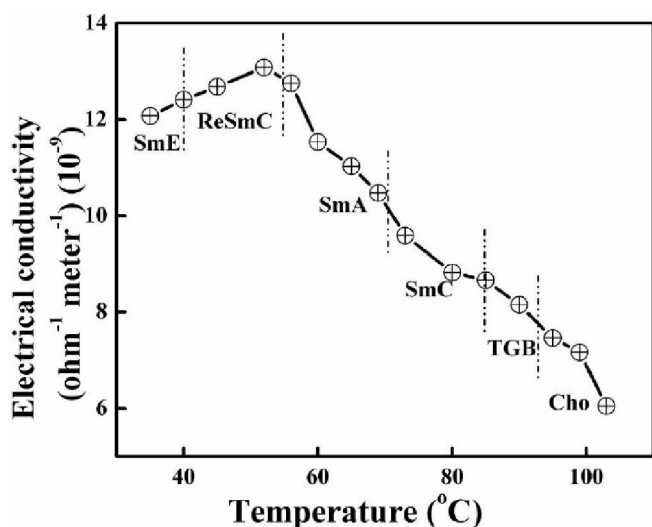


Figure 3 : Temperature variation of electrical-conductivity  $\sigma$  ( $\times 10^{-9} \Omega^{-1} \text{ m}^{-1}$ ) for the sample of 45% of BBHA in CN

of behavior is generally observed in hexagonal, cubic and lamellar phase of lyotropic and thermotropic systems<sup>[17-19]</sup>.

### Thermodynamic studies

Study of liquid crystalline mixtures is important not only from the viewpoint of their technological applications but also from that of fundamental studies in the field of molecular interactions<sup>[20]</sup>. Thermodynamic studies are a very important role to understand the phase stability, chemical structure and dynamics of liquid crystals<sup>[21, 22]</sup>. Temperature dependent molecular orientations of liquid crystalline phases have been considered in many technological applications. The applied applications of these technologies are based on the properties of molecular structure and intermolecular interactions. The intermolecular forces such as van der Waals interaction, hydrogen bonds, electron donor interactions and steric repulsive interactions are they individually or together may be responsible for increasing or decreasing the thermal stability of liquid crystalline phase<sup>[23]</sup>. Thermodynamical variations of liquid crystalline phase at different concentrations of binary mixtures of liquid crystalline materials are estimated using Boltzmann distribution laws. Draw a graph of variations of density as a function of mole fraction for the sample of BBHA in CN at constant temperature 50 °C is presented in Figure 4, which clearly

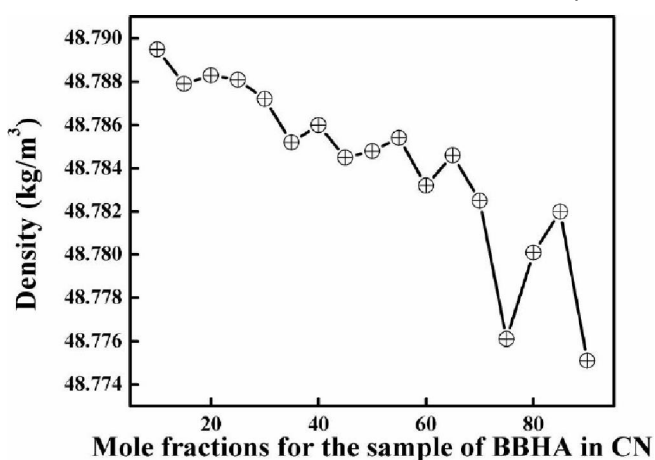


Figure 4 : Variations of density as function of mole fraction for the sample of BBHA in CN

shows, the degree of microphase separations are one of the parameters to controlling a physical properties of liquid crystalline materials<sup>[24]</sup>. In this context the existence parameter can be varied infinitesimally small either through chemical modification or through physical modification and hence they are depends on nature of additives molecules. The figure clearly illustrates that, statistically how the molecular interactions are thermodynamically changes at different concentrations in order to show the thermal stability of liquid crystalline phase. Here we noticed that: the magnitude of spin temperature dependent molecular orientation is restrained and then it varies from concentrations to concentrations and hence it also changes the intermolecular energy of given molecules. The molecular density of mesosphere, charges on molecules represent an electrostatic molecular interaction, but they do not show the real charge distribution in molecule. The molecular ordering or the phase stability of liquid crystalline phase at constant temperature: the intermolecular interactions are responsible for the charges of carbon and the adjacent hydrogen molecules and which shows the correct electrostatic potentials are reproduced by different partial charge distributions. Either increasing or decreasing the mole fraction; which cause a small variation of electrostatic potentials and which they around the molecule. In spite of these uncertainties, the full set of partial charges is very useful, as it can provide a detailed insight into the molecular arrangement in mesophases and they reproduce the electrostatic potential very well.



## CONCLUSIONS

The salient features of this investigation are the following: The existence of twisted grain boundary (TGB) and re-entrant smectic-C (ReSmC) phases have been observed by using microscopic technique in binary mixture of BBHA in CN. The temperature variations of density across cholesteric and smectic-E phases are more predominant than the other transitions. Drastic changes in the values of electrical-conductivity with the variation of temperature unambiguously correspond to molecular orientations of Cho-TGB-SmC-SmA-ReSmC-SmE phases at different temperatures. Changes in electrical-conductivity are expected to be due to changes in the dimension of discs along with changes in the orientational order of the molecule. But below a particular temperature, the size of aggregates becomes so large, that the specimen moves towards crystalline nature. Thermodynamic studies have also been discussed to understand the phase stability, chemical structure and molecular dynamics of the binary mixture of liquid crystalline materials.

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