

Thermo-optical and electro-optical response of binary mixture of liquid crystalline materials

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ABSTRACT

We report the results of our studies on the optical, thermal and electro-optical properties of binary mixture of cholesteric and nematic compounds: namely, p-butoxybenzylidene, p-heptylaniline (BBHA) and cholesteryl nononate (CN). The mixture exhibits very interesting twisted grain boundary (TGB) phase and re-entrant smectic-C (ReSmC) phases sequentially when they are cooled from its isotropic melt. Optical and electro-optical studies have been discussed. © 2016 Trade Science Inc. - INDIA

KEYWORDS

Binary mixture;
Optical studies;
Density and ultrasonic
measurements;
Adiabatic compressibility;
Electro-optical studies.

INTRODUCTION

Increasing technological applications^[1] of liquid crystals are attracting both physicists and chemists in understanding their basic structure. The study of density in liquid crystals provides useful information regarding various phases and phase transition^[2]. Ultrasonic velocity studies of the liquid crystals provide additional information and confirmation about the different phases and phase transitions^[3-5].

In the present investigation, our aim is to carry out the study of different properties of binary mixture of liquid crystalline materials^[6,7]. Some of the concentrations of given mixtures exhibits a twisted grain boundary (TGB) phase and re-entrant smectic-C (ReSmC) phases sequentially when they are cooled from its isotropic melt. Optical and electro-optical studies 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

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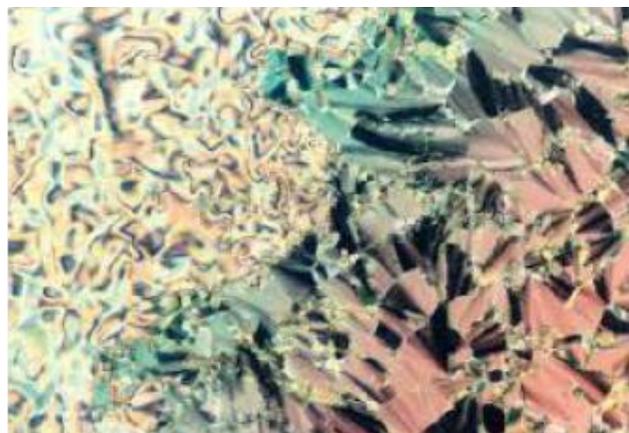
density measurements was $\Delta\rho = \pm 0.0001$ g/cc. The ultrasonic velocity was measured at 2 MHz using the ultrasonic interferometer UI 601 NPL India. The cell was essentially the same as that supplied with the interferometer except a few modifications for the heating arrangement. The temperature of the cell was controlled by controlling the current flowing through the heating element surrounding the cell. The permitted temperature control was $\pm 0.2^\circ\text{C}$. The ultrasonic velocity measurements were accurate to $\pm 0.2\%$. Electro-optical measurements were carried out by the usual experimental setup of Williams^[8]. It consists of tin oxide coated transparent conducting glass plate and the sample sandwiched between these two glass plates. Teflon spacers having thickness of $d=39 \pm 1 \mu\text{m}$ were used and observations were made at 90°C using polarizing microscope in conjunction with a hot stage.

RESULTS AND DISCUSSIONS

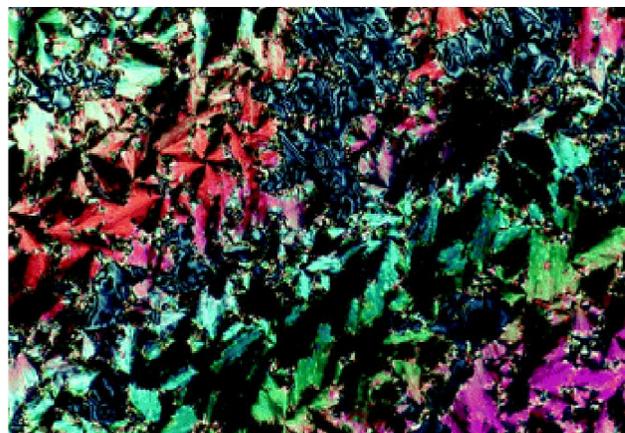
Optical texture studies

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^[9,10]. 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^[11,12]. On further cooling, thread-like TGB phase changes over to appearance of tilting the molecules are relative to smectic layers and then it is the characteristics of well defined schlieren textures of SmC as shown in Figure 1(a). On further cooling the specimen, SmC phase may transform into the focal conic fan shaped texture of SmA and it as shown in the Figure 1(b). Molecular structural confirmations of SmA phase is stable at temperature 60°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^[13]. 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



(a) Schlieren texture of SmC phase (180X)



(b) Focal conic fan shaped texture of SmA phase (180X)

Figure 1 : Microphotographs showing

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^[14]. 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-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^[15,16].

Density measurement

The temperature variations of density for 45% BBHA in CN as shown in the Figure 2, which clearly illustrates that: the density increases linearly with decrease of temperature in the region of isotropic-crystalline phase of given mixture. The phase transition is very near the isotropic liquid- cholesteric transition a sudden jump in density is observed. The jump in density shows the increasing value and hence it indicates that: isotropic-cholesteric transition is probably first order. The sudden jump in density at the transition is attributed to a sudden change in the molecular structure from the disordered isotropic to the ordered cholesteric phase. The higher values of density in the cholesteric phase than that of in isotropic region indicate the tendency of increasing order with decrease of temperature is more in the cholesteric phase Pretransitional effects at the isotropic-cholesteric transition are found to observed

on the lower side of the transition^[17,18], which supporting the Maier-Saupe theory^[19]. After the isotropic transition, density increases linearly with decrease of temperature in the cholesteric phase. At cholesteric-TGB transition the density shows a sudden raise. The measured higher value of density and thermal expansion coefficient indicate that: the transition is first order. Our measurements are in accordance with Torza and Cladis' on CBOOA. Density increases linearly with decrease of temperature in the TGB phase. The increasing density is observed at Smectic-C–Smectic-A- ReSmectic-C–Smectic-E transitions. The measurement of increasing density across this transition is more predominant than the other transitions.

The temperature variations of ultrasonic velocity, adiabatic and molar compressibility

The mixtures of liquid crystalline materials due to their unusual behaviors have attracted considerable attention. Ultrasonic velocity measurements also help in the study of phase behavior with temperature^[20]. As the orientational order of the molecules in mesomorphic compound changes with increasing the concentration of one more additive substance and hence, the attractive force between the components of the molecules, the measure of ultrasonic velocity, absorption should give the nature of attractive forces existing between the mixtures of the given molecules. Data on some of the properties associated with refractive index, ultrasonic velocities and surface tension find extensive application in chemical engineering process, simulation and

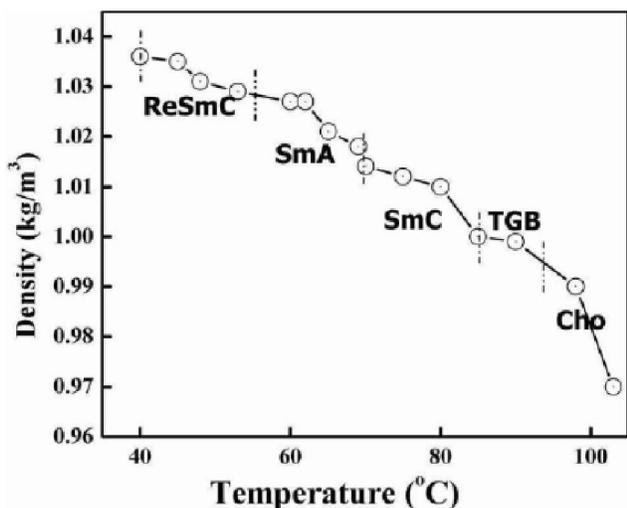


Figure 2 : Temperature variations of density for the sample of 45% BBHA in CN.

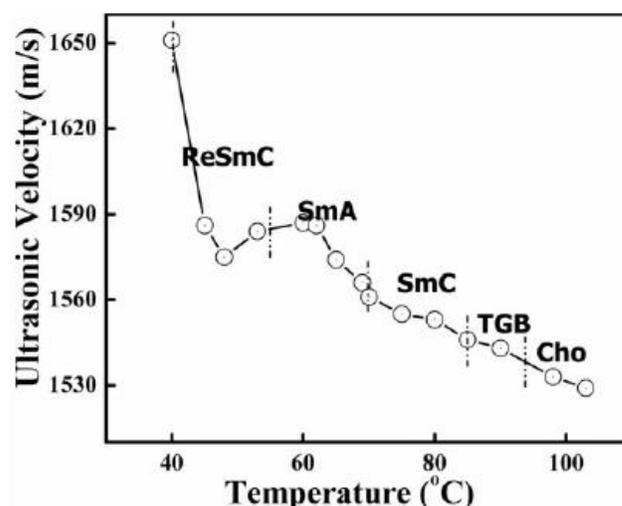


Figure 3(a) : The temperature variation of ultrasonic velocity for the sample of 45% of BBHA in CN

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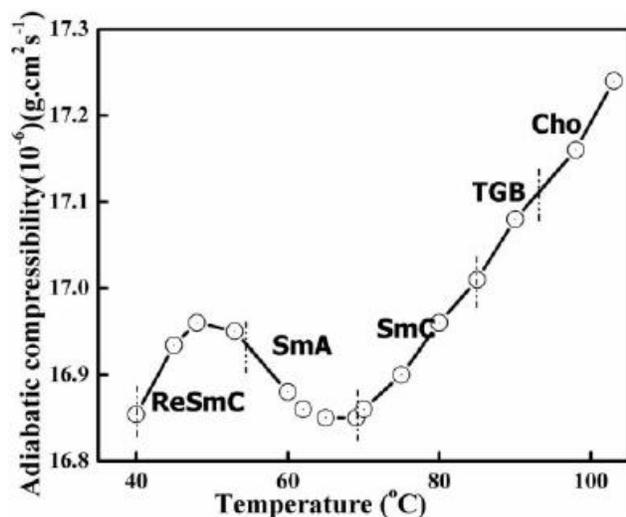


Figure 3(b) : The temperature variation of adiabatic compressibility for the sample of 45% of BBHA in CN

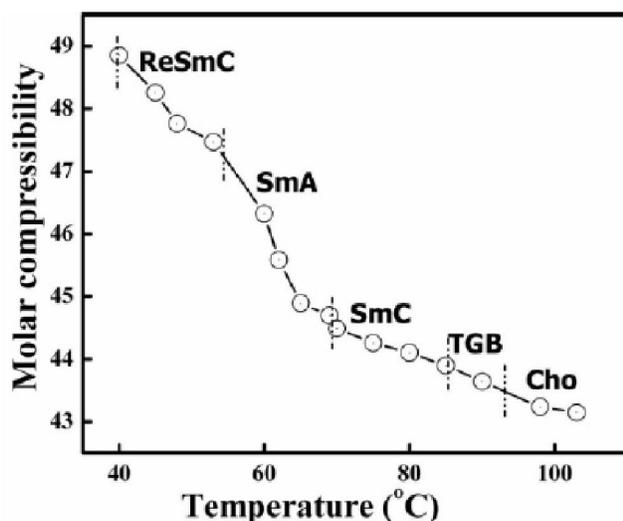


Figure 3(c) : The temperature variation of molar compressibility for the sample of 45% of BBHA in CN.

molecular dynamics^[21]. The temperature variation of ultrasonic velocity, adiabatic compressibility and molar compressibility in the present case is shown in Figures 3(a)-(c). The velocity exhibits an anomalous behavior at the isotropic mesophase transition while it varies linearly in the isotropic and mesomorphic phases away from transition. The velocity shows a dip at the transition. The ultrasonic velocity linearly increases in isotropic phases up to the transition with decreasing temperature^[22,23]. The increase in velocity is explained as the decrease in mean distance between the molecules, thereby increasing the potential energy of the interaction between the molecules. The velocity reaches a minimum at the transition temperature and increases sharply below the transition, and then it shows a linear increase in

mesophase. The change in velocity and other parameters^[24] at the transition results from disordered molecular arrangement in isotropic phase to an ordered arrangement of molecules in the liquid crystalline phase with long-range orientational order^[25]. The variation of adiabatic compressibility^[26] is remarkably linear in the isotropic and mesomorphic phases, but it shows a step jump at the isotropic-mesophase transition. The result of molar compressibility varies linearly with temperature at the isotropic phase transition. In this study, the higher values of thermal expansion coefficient in mesophase than in the isotropic phase confirm the tendency of increasing order of molecule with decrease in temperature. It is firmly established that the ultrasonic velocity and the related parameters^[27] are structure dependent. Besides, depending on the structure, they are related to intermolecular interactions and degree of molecular order in liquid crystalline mixture. It is well known that in liquid crystalline phases, the molecules are arranged in order and the orderliness increases from isotropic to Cho, TGB, SmC, SmA, ReSmC and SmE phases. The twisted grain boundary (TGB) phase and re-entrant smectic-C (ReSmC) phases are known to exhibit in this polymorphism at different temperature and at different concentrations of the given molecules compared to other conventional liquid crystalline phases such as cholesteric, SmC, SmA and SmE phases^[28,29].

Electro-optical studies

Electro-optical measurements are very important tool in getting better idea on the phase transition behavior of liquid crystalline phases with electric field at constant temperature. In this study we have been considered the sample for mixture of 45% of BBHA in CN at constant temperature 90 °C. When the applied voltage increases: the structural molecular arrangements of liquid crystalline phases start to fluctuate and begin to grow and hence it deforms gradually the original position of the structural formations. Remarkably it has been observed that, if at constant temperature, the various aspects of low frequency effects on given mixture clearly shows different directions of molecular orientations/re-orientations and hence it forms a flow patterns: such as stripped pattern and chevron textures. The formations of zig-zag and herringbone patterns are characteristic of chevron textures and also the forming

time of these patterns depends on applied electric field. If there we have been observed a significant difference of electro-mechanical responses of these textures and the stripes of these textures do not have a linear electro-mechanical effect at low fields and at higher fields it shows mechanical vibration. This indicates that the spontaneous polarization has rotated and is no longer parallel to the electric fields. In contrast to the director: the molecular orientations/re-orientations of the layer structures are unchanged by the application of applied electric field. Sequentially if we have to increase the applied field above 22.20 V and hence the microscopically observed structural pattern becomes dynamic scattering mode-like and also it has been appearing like an irregularity of molecular orientation/re-orientations of frustrated liquid crystalline phase. The frustrated liquid crystalline phase is arises in that regions, which are probably due to the structural molecular orientations/ re-orientations are not being confirmed in X, Z plane. When the applied filed is kept at constant: microscopically we have been observed a completely stationary and regular arrangement of two-dimensional hexagonal grid pattern texture and these hexagonal grid pattern textures are presented in Figure 4. The hexagonal grid pattern textures are gradually deforms with increasing frequency and hence at some stage, it becomes indistinguishable from the chevron texture. However: the hexagonal grid pattern is rather stationary and is formed in a short time at 250Hz, 23V. From this figure: it follows that: an extremely regular arrangement

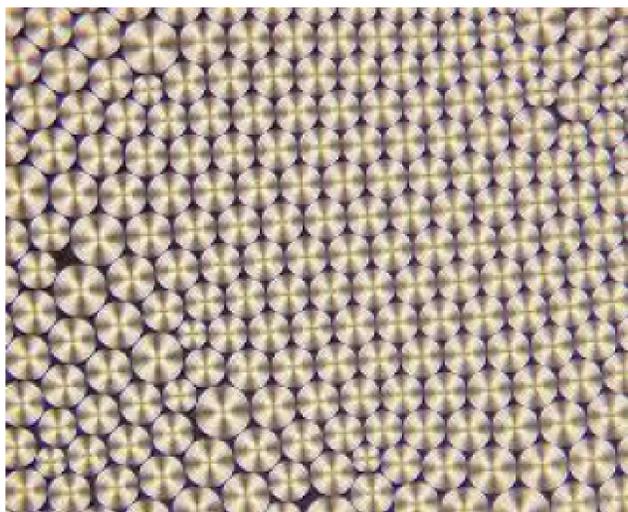


Figure 4 : Hexagonal grid pattern electro-optical texture obtained at temperature 90 °C.

of two-dimensional hexagonal grid pattern texture is formed by the applied field. One of the regions is that: the formation of hexagonal grid pattern texture is the electronic charge injected by the applying external electric field^[30-33].

CONCLUSIONS

The salient features of this investigation are the following: The existence of twisted grain boundary (TGB) and re-entrant smectic-C phases have been observed by using microscopic technique in binary mixture of BBHA in CN. The temperature variation of density across the cho-TGB-SmC-SmA-ReSmC-SmE is more predominant than the other transitions. The anomalous behavior of liquid crystalline physical properties, such as ultrasonic velocity, adiabatic compressibility, and molar compressibility, is discussed at the isotropic mesosphere transition. Under the applied electric field at constant temperature unambiguously correspond to optical purity of the liquid crystalline phases. The various aspects of frequency effects on the given mixture show different directions of molecular reorientations exhibit a flow patterns formed such as stripped pattern chevron textures and hexagonal grid pattern textures, and hence these textures microscopically have been observed.

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