

STUDIES OF THE CHROMONIC PHASES OF LIQUID CRYSTALS USING SURFACE MORPHOLOGY AND OPTICAL TRANSMITTANCE**V. Sivaprasad¹ and T.N. Govindaiah²**¹Department of Physics, Government First Grade College, Channapatna-562160, Karnataka, India²Post-Graduate Department of Physics, Government College (Autonomous), Mandya-571401, Karnataka, India¹varakuti@gmail.com and ²tngovi.phy@gmail.com**ABSTRACT**

In this present paper main focus is on the thermal and optical characteristics of a system made up of two binary components: berberine and 4-n-(nonyloxybenzoic) acid (NOBA). When the specimen is cooled from its isotropic phase at varying temperatures, the mixture of these molecules exhibits the chromonic phases of the co-existing biphasic area of the isotropic nematic (N+I) and lyotropic nematic (N+C) phases, respectively. The temperature-dependent refractive index of liquid crystalline samples as determined experimentally is clarified in this work. Optical-birefringence was used to estimate the intermolecular interactions of tilted chromonic molecules in the N+I and N+C phase area. Understanding the potential energy of interaction between the chromonic phases of tilted molecules is aided by experimental investigations of temperature variations of optical density, ultrasonic velocity, and optical transmittance measurements.

Keywords: Optical studies: Birefringence: Chromonics: ultrasonic measurements: optical transmittance:

INTRODUCTION

Liquid crystals are anisotropic fluids that exhibit mesophases at specific temperatures between the crystalline solid and amorphous liquid states. There is no positional ordering in the molecule, but there is orientational ordering. As a result, the mesophases are merging to create a liquid-like flow behavior and anisotropic physical characteristics. Photonic crystals are employed in numerous industrial technological applications of liquid crystalline displays, and tuning the semiconducting energy band gap is beneficial. One of the key remedies for the sensible semiconductor energy band gap of liquid crystal displays is a change in the values of effective optical-refractive indices. Among the components of photonic crystals are liquid crystals, such as chromonic or nematic, dyes, drugs, and nucleic acids [1-3].

Lydon recently provided two good assessments that outline the current level of knowledge surrounding the chromonic compounds. Since the hydrophilic groups that give the chromonic molecules their water solubility are dispersed across the hydrophobic aromatic rings' periphery, the hydrophilic and hydrophobic components cannot be clearly distinguished. The chromonic molecules do not form micelles as a result, although they may exhibit a noticeable amount of surface activity. On the other hand, these molecules' planar aromatic Π -rings create a favorable Π - Π contact which results in a face-to-face stacking of the rings.

The way the molecules stack together creates aggregated columnar chromonic phases, which indicates whether the molecules were produced in isotropic fluids. A column stacking that is uniaxial and devoid of positional order is associated with the isotropic nematic N+I phase. Higher concentrations also cause the columns' orientational and positional arrangement to exhibit a hexagonal intermediate M phase. The birefringence values of liquid crystal materials were assessed to be low and medium ($\Delta n = 0.09/0.12$) and high (0.2 to more than 0.5) for the purposes of liquid crystal display applications.

The temperature has a significant impact on the effective optical birefringence values of nematic liquid crystals. Similar to the clearing temperature, the appearance of liquid crystals changes to an isotropic condition where there is no molecular organization. External electric or magnetic fields can affect the director of nematic liquid crystals, changing the effective refractive index values. A major factor in the creation of new liquid crystal mixes is the response of the optical anisotropy of the energy gap or the semiconducting qualities of the band structure of the energy gap of liquid crystalline materials, which are caused by variations in the values of lower or higher

birefringence. Nematic crystals' optical birefringence values have been widely employed in a variety of applications, including switchable phase shifters, tunable spatial modulators for light and laser beam steering and holography, various tunable filters that remove or select bands, tunable capacitors, antennas, and lenses, as well as other devices like photonic fiber [4–9].

The present work shows that different amounts of these molecules indicate the presence of co-existing biphasic zones of lyotropic nematic (N+C) and nematic (N+I) phases at different temperatures. These phases have been documented by the use of the microscopic method. To comprehend the optical anisotropy of the chromonic phase of liquid crystals, optical and thermal investigations were carried out [10, 11]. It has been discussed how slanted molecules interact with one another in the N+I and N+C phase regions. There has also been discussion of how temperature affects optical-density, and optical transmittance measurements.

EXPERIMENTAL SECTION

In the present study, we use the molecular compounds, namely: 4-n-(nonyloxybenzoic) acid (NOBA) and berberine. Using benzene as a solvent it was subjected to purification twice by adopting the method of re-crystallization. For our experimental studies, we have considered the binary system of 4-n-(nonyloxybenzoic) acid (NOBA) molecules are at 40% of concentration and 60% concentration of berberine molecules. To ensure homogeneity the ratio of given mixtures in desiccators is kept in exposures to many cycles of heating, stirring and centrifuging. Transition temperatures of given concentrations were measured using a Gippon-Japan polarizing microscope in conjunction with a hot stage. For microscopic observations the samples take their place on slide. Refractive indices in the optical region were determined at different temperatures using multi-wavelength Abbe-refractometer (Atago:DR-M4) including constantly circulating constant bath and six interference color filters. The permitted temperature control was $\pm 0.1^\circ\text{C}$. The level of liquid crystal in the capillary was read to ± 0.01 mm with a cathetometer. The absolute error in the density measurements was $\Delta\rho = \pm 0.0001$ g/cc. For the optical transmittance measurement, the sample was in to the standard sample holder pretreated for planar alignment having $5\ \mu\text{m}$ spacer by heating it 10°C above the clearing point of the sample and then introducing the sample at one end of the holder it was filled in the sample holder by the capillary action and sample holder was slowly cooled up to the room temperature. Now sample holder is placed between two crossed polarizer of polarizing microscope model CENSICO (7626) fitted with a hot stage and light intensity coming through the eye-piece has been measured by light-dependent resistance (LDR). The resistance value of LDR corresponding to varying light intensity due to temperature variation of the sample is proportional to the inverse of optical transmittance and has been directly measured by attached digital multi-meter.

THEORETICAL ANALYSIS

GENEARAL THEORY ON POLARIZABILITY

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

$$\vec{D} = \epsilon_0 \vec{E} + \vec{P}$$

Since

$$\vec{D} = \frac{q}{A} = \frac{\epsilon_0 \epsilon_r q}{A \epsilon_0 \epsilon_r} = \epsilon_0 \epsilon_r \vec{E} = \epsilon \vec{E}$$

Where

$$\epsilon = \epsilon_0 \epsilon_r$$

Therefore

$$\epsilon \vec{E} = \epsilon_0 \vec{E} + \vec{P}$$

$$\vec{P} = \epsilon_0 \epsilon_r \vec{E} - \epsilon_0 \vec{E} = \epsilon_0 \vec{E} (\epsilon_r - 1)$$

$$(\epsilon_r - 1) = \frac{\vec{P}}{\epsilon_0 \vec{E}}$$

Where ϵ_r is the electrical susceptibility of the liquid crystalline material medium.

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

$$\vec{\mu}_e = \alpha_e \vec{E}$$

Where α_e is called electronic Polarizability.

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

$$\vec{P}_e = N \vec{\mu}_e = N \alpha_e \vec{E}$$

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

But
$$\vec{P}_e = \epsilon_0 \vec{E} (\epsilon_r - 1)$$

Therefore

$$\epsilon_0 \vec{E} (\epsilon_r - 1) = N \alpha_e \vec{E}$$

or
$$(\epsilon_r - 1) = \frac{N \alpha_e}{\epsilon_0}$$

RESULTS AND DISCUSSIONS

LIQUID CRYSTALLINE PROPERTIES

The molecular orientations of optical textures of chromonic phases of liquid crystal mesophases were observed using a hot-stage Gippon-Japan-polarizing microscope. The sample consisted of a binary mixture of thermotropic/lyotropic liquid crystals, specifically 4-n-(nonyloxybenzoic) acid (NOBA) and berberine. The chromonic character of optical texture is depicted in Figure 1, where a co-existing biphasic area of the nematic (N+I) phase causes an induced phase transition. A co-existing biphasic area of chromonic molecules that is visible under a microscope has noticeable surface activity but does not form micelles.

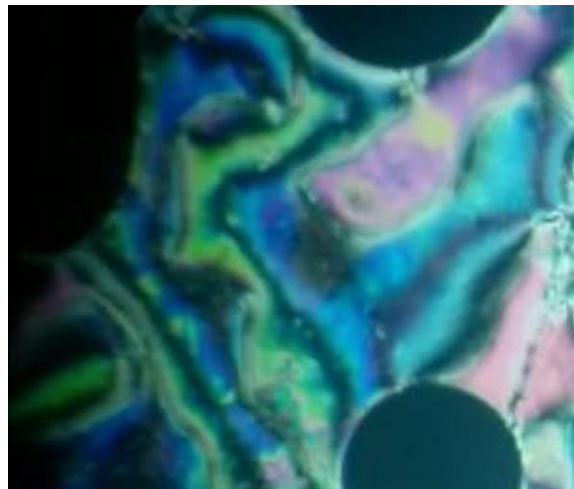


Figure 1: Microphotographs showing, Co-existent biphasic region of nematic (N + I) phase.

However, the antibacterial capabilities of berberine molecules tend to stack when NOBA molecules are present because of the hydrophobic effect and weak Van der Waals contacts between the cores [12, 13]. As the specimen cools further, this phase transitions to a lyotropic columnar nematic (N+C) phase at varying temperatures and persists until it approaches room temperature. It is important to note that at low temperatures, the segregation of columnar nematic molecules increases with varying quantities of the supplied molecules. In order to decrease molecular self-assembly of nematic molecules, the aggregated size of given molecules often grows as the temperature drops, giving the illusion of increased entropy. It is the result of molecular motion inside the anisotropic medium and is a feature of a thermodynamic system. The amount of stored kinetic energy is represented by the entropy. The stability of chromonic phases, which is dependent on both temperature and concentration, is demonstrated by the several forms of stored kinetic energy.

SCANNING ELECTRON MICROSCOPY (SEM)

The SEM was used to analyze the surface morphology of a binary mixture of liquid crystalline materials, specifically 4-n-(nonyloxybenzoic) acid (NOBA) and berberine molecules, at an accelerating voltage of 15 kV. According to the SEM, the increased surface energy caused the agglomerated particles of the mixture to form polymer strands and topographical structures that resembled rice grains when they arranged side by side, as seen in Figure 2(a, b). Understanding the nature of the functional moiety and the flexibility of the chains connected to the mesogenic core has been made possible by the surface morphology of these images. These images' structural characteristics can be utilized as building blocks to create optically desirable liquid crystals [14, 15].

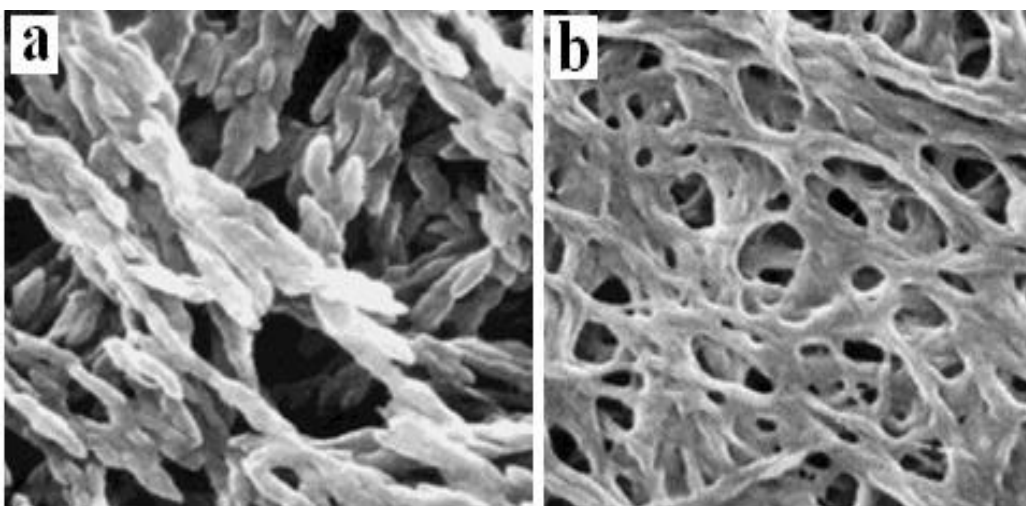


Figure 2: SEM images showing the rice grain-like structures and polymer strands.

OPTICAL ANISOTROPY OF BIREFRINGENCE STUDIES

Crystals are the best-characterized birefringent materials. The refractive indices are clearly characterized because of their distinct crystalline formations. Numerous bio-based crystals, polymers, and liquid crystalline materials are available, and their significant industrial uses have been widely documented. A substance with two refractive indices is said to exhibit birefringence, an optical property that is dependent on the polarization and direction of light transmission. A substance that possesses this characteristic is referred to be birefringent. The optical analyses of binary/ternary mixes with varying proportions of liquid crystalline components provide additional support for the findings of this experiment. Here, we used a multi-wavelength Abbe-refractometer set to 589.3 nm in order to measure the temperature variation of the refractive indices (n_e and n_o) for the mixture of varying concentrations of 4-n-(nonyloxybenzoic) acid (NOBA) and berberine molecules in the presence of co-existing biphasic regions of nematic (N+I) and lyotropic nematic (N+C). It has been established that the refractive index is n_e owing to extraordinary rays and n_o due to regular rays. Figure 3 displays the temperature changes of optical-birefringence for 40% of NOBA molecules combined with berberine.

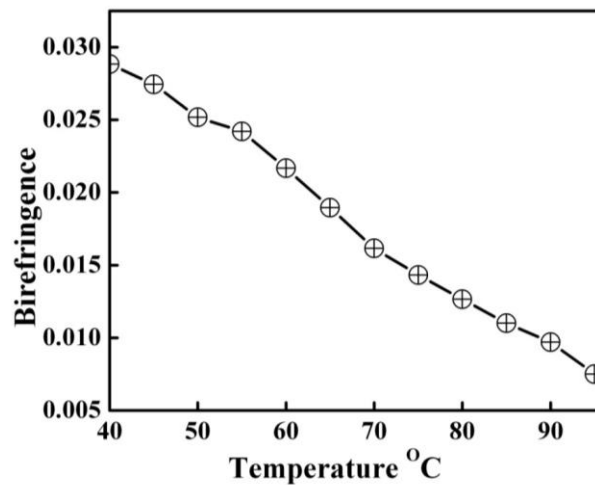


Figure 3: The temperature variations of optical-birefringence for 40% of NOBA in berberine.

The figure shows that the birefringence values change significantly wherever there is an isotropic–liquid crystalline phase transition. This clearly shows that the changes correspond to isotropic-nematic (N+I) and lyotropic nematic (N+C) phases at different temperatures. Additionally, as the concentration of NOBA molecules increases, the optical-birefringence values drop with temperature because the molecules' effective optical anisotropy also decreases [16-18].

DENSITY MEASUREMENT

The ordering of liquid crystals can be described using the positional order parameters. The variation in the density of liquid crystalline molecules best describes it. Figure 4 in this study's temperature changes of density for the 40% NOBA in berberine sample makes it abundantly evident that, in the optical area between the isotropic and crystalline phases of the present mixture, density increases linearly with decreasing temperature [17, 18]. The phase transition is much closer to the isotropic and biphasic regions of the nematic (N+I) phase area; at this point, a sharp increase in density values has been noted. 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 co-existent biphasic region of nematic (N+I) 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.

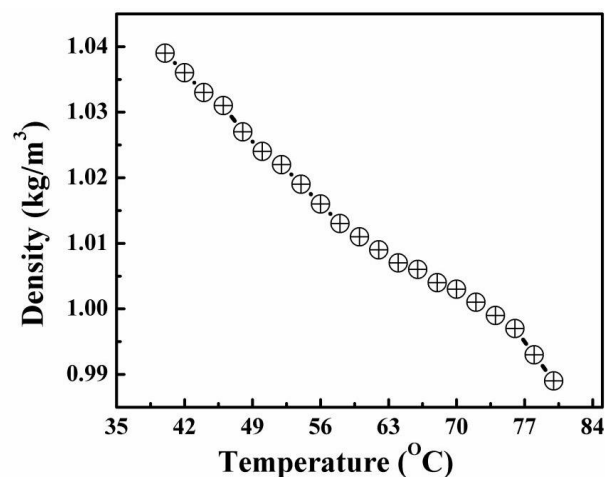


Figure 4: Temperature variations of density for the sample of 40% of NOBA in berberine.

According to Maier-Saupe theory [19, 20], pre-transitional effects at the optical region between the isotropic and biphasic region of nematic (N+I) phase transitions are found to be observed on the lower side of the transition. The higher density values in the (N+I) phase region are greater than those in the isotropic region, which clearly indicates that the tendency of increasing molecular order is greater with decreasing temperature. Following isotropic transition, the density of the given mixtures increases linearly with decreasing temperature at the biphasic region of the nematic (N+I) phase region. At the optical region between the co-existing biphasic region of the nematic (N+I) \rightarrow lyotropic nematic (N+C) phase transition, the density values exhibit an increasing nature. The phase transition is first order, as indicated by the measured higher values of the density and thermal expansion coefficient. Our measurement experiments are consistent with the work done on the molecules CBOOA by Torza and Cladis [21-22]. As the temperature drops, the densities of the specified combinations progressively rise toward the lyotropic nematic phase. Increasing densities have been experimentally found in various optical regions as the temperature drops near the crystalline phase. Density measurements at various optical areas are more common than those at other optical regions.

OPTICAL ANISOTROPIC STUDIES ON MOLECULAR DYNAMICS

The structure and dynamics of macromolecules, including as medications, proteins, and nucleic acids, have been extensively studied using molecular dynamics. Since computer technology has advanced so dramatically, molecular dynamics has become a crucial tool for describing the structure, dynamics, and organization of molecules as well as for examining the thermodynamical and molecular characteristics of ordered systems. These systems contain molecules in the form of smooth, anisotropic, soft, and stiff particles. As illustrated in Figure 5, the molecular layer spacings as a function of temperature-dependent birefringence of various liquid crystalline phases for the 40% NOBA in berberine sample explain the relationships between the wavelength of optical textures, molecular layer spacings, and birefringence of the given molecules at various temperatures in the region of existent co-existent biphasic region of nematic (N+I) and lyotropic nematic (N+C), respectively. This study has yielded several important findings, and we have seen that reactive mesogens are getting close to creating molecular layers with favorable transport characteristics that are accessible throughout the temperature range between the co-existing biphasic region of lyotropic nematic (N+C) and nematic (N+I) phases. Interestingly, it demonstrates that the birefringence values for a certain mixture rise at specific wavelengths of optical textures of molecule tilt in relation to the changes in layer spacing [23]. It is possible to utilize liquid crystalline materials as thermometers in this temperature range due to the phenomenon of changes in birefringence with temperature. The reflected color of the material indicates the temperature of its surroundings. Additionally, it can be utilized to develop sensors that react to temperature changes in a number of ways. The solid material is white with various aggregation phases when it has consolidated at room temperature. After placing the provided sample under a polarizing microscope, the optical textures were noted. The samples resulting intensity distribution, caused by polarized light interference, is represented by the bright and dark patches. distinct twist states are also associated with distinct hues that are observed between crossed polarizers [24-26].

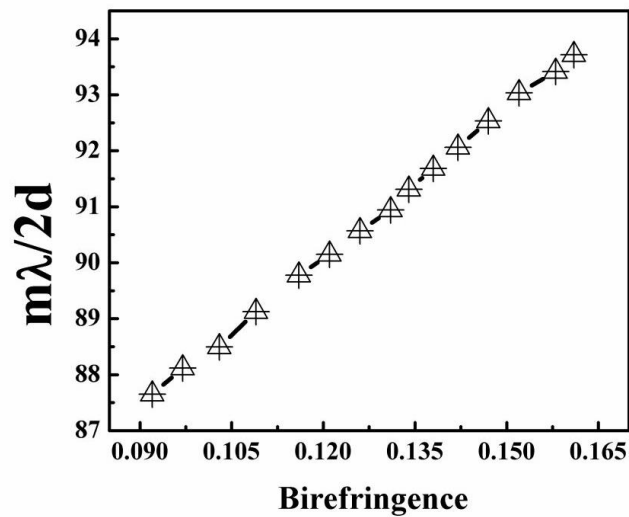


Figure 6: Variation molecular layer spacing's as function of temperature dependent birefringence for the given sample of 40% of NOBA in berberine

OPTICAL TRANSMITTANCE STUDIES

Optical transmittance is one of the important parameters for liquid crystalline studies. Characterizations of this liquid crystal mixture study are very crucial for photonic devices, opto-electronic, electro-optical, and display technologies. Depending on the chemical configuration, this system relates to one or more distinct mesophases, such as nematic (N), cholesteric, smectic, TGB, and chromonic phases at various temperatures. It also refers to the amount of light transmitted to an optically transparent anisotropic medium. Figure 7 displays the temperature change of optical transmittance for samples containing 40% NOBA in berberine. This clearly shows that, while the sequence of phases appears from the crystalline region to the near isotropic region, and that there are abrupt changes in the value of optical transmittance from 68°C to 80°C, the value of optical transmittance increases gradually with temperature from 40°C to 68°C [27,28]. At the co-existing biphasic region of the nematic (N + I) phase transition and the lyotropic nematic (N + C) phase, the optical transmittance is continuous. The molecular orientations of the various liquid crystalline phase transitions are not energetic, as can be observed here. As the temperature rises, the optical transmittance falls, and it diverges as it gets closer to the co-existing biphasic area of the nematic (N + I) phases.

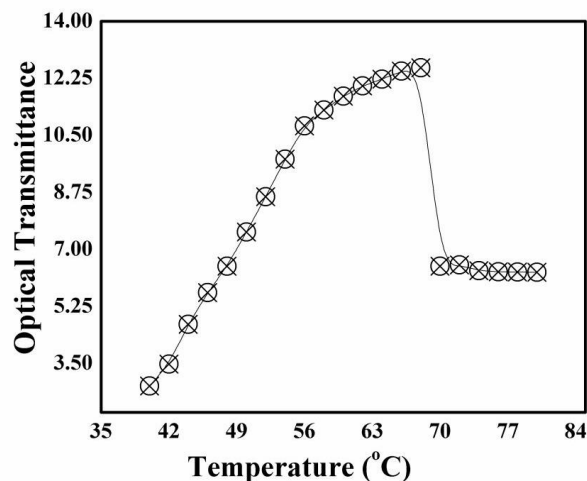


Figure 7: Temperature variation of optical transmittance for the given sample of 40% of NOBA in berberine

The divergence of optical transmittance can be related to the first-order transition. Here in the region of co-existent biphasic region of nematic (N + I) phase, the optical transmittance shows a steep decrease and it is very nearer to isotropic region: it is one of the important point to observe the phase transition by detecting the enthalpy change associated with it and also by measuring the level of enthalpy changes, from this enthalpy studies we can able to learn the type of the phase transition[23], which is the characteristic of first-order transitions of co-existent biphasic region of nematic (N+I) phase respectively at different temperatures.

CONCLUSIONS

It is evident from optical microscopic analyses of a binary mixture of NOBA and berberine molecules that, for specified concentrations and temperatures, there are co-existing biphasic areas of nematic (N+I) and lyotropic nematic (N+C) phases. Rice grain-like structures and polymer strands are the basic features of surface morphology in SEM pictures. They have also highlighted the structural characteristics that may be used to comprehend the structures and constituents of the chromonic liquid crystalline phase with optical properties. Compared to the other phase transitions, the temperature change in density throughout the biphasic areas of the lyotropic nematic (N+C) and nematic (N+I) phases is more pronounced. The optical region of chromonic phases at various temperatures has also been explored in relation to the intermolecular interactions of tilted molecular layer spacing's. The potential energy of interaction between the chromonic molecules can be better understood by using the characteristics of optical transmittance.

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