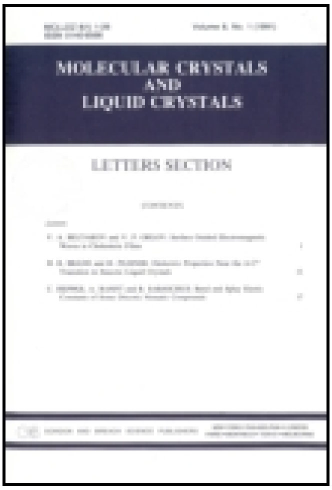

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Co-Existent Biphasic Region of Nematic and Columnar Smectic Phases in Binary Mixture of Berberine and Alizarin Dye

T. N. Govindaiah[a], H. R. Sreepad[a] & Nagappa[b]

[a] Post-Graduate Department of Physics, Government College (Autonomous), Mandya, India

[b] Department of Physics, University of Mysore, Manasagangotri, Mysore, India

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T. N. GOVINDAIAH,[1,*] H. R. SREEPAD,[1] AND NAGAPPA[2]

[1]Post-Graduate Department of Physics, Government College (Autonomous), Mandya, India
[2]Department of Physics, University of Mysore, Manasagangotri, Mysore, India

We report the results of our studies on the optical and thermal properties of binary mixture of two compounds viz., berberine and alizarin dye. The mixture shows a very interesting co-existent biphasic region of nematic N + I and smectic C + I phases, sequentially when the specimen is cooled from its isotropic phase respectively at different concentrations of Alizarin dye in berberine molecule. The temperature variations of optical anisotropy, optical textures, and electrical conductivity have also been discussed. Aggregated molecular size has been confirmed by X-ray studies.

Keywords Binary mixture; columnar phase; lyotropic chromonic; molecular aggregation; nematic; optical anisotropy

Introduction

During last 40 years, a lot of research and development has been done in the field of liquid crystals for their use in display applications. The important features required for this application are flatness, low power consumption, compactness leading to low weight, and full color capability [1]. The liquid crystalline display [2] that uses a liquid crystal and dye mixture has received much more attention because of its wide viewing angle, daylight readability, high brightness, and no requirement of polarizers. Dye-doped liquid crystals have received substantial interest in the recent decade in the development of optical applications owing to their high birefringence and highly flexible optical controllability via manipulation of the interaction of liquid crystals with the photoexcited dyes [3–5].

The microscopic mechanisms are not still clearly understood and quite often experimental results still reveal unexpected behaviors [6–9]. The addition of dyes into nematic liquid crystals, even in small concentrations, introduces new orienting mechanisms [6]. Mixing of carbon nanotubes in liquid crystal host is the recent development toward the modification of physical properties of liquid crystals by doping non-mesogenic molecules [10,11].

In the present work, we have considered the mixture of alizarin dye and berberine molecules. The polymorphic co-existent biphasic regions of nematic – N + I and aggregated columnar smectic – C + I phases have been observed using optical microscopic technique,

*Address correspondence to T. N. Govindaiah, Post-Graduate Department of Physics, Government College (Autonomous), Mandya 571401, India. E-mail: tngovi.phy@gmail.com

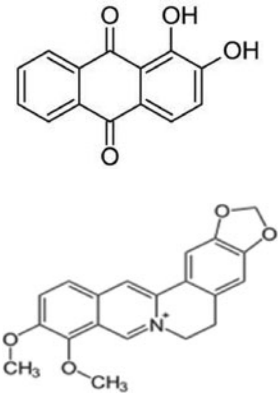

Figure 1. (a) The structural formula for alizarin dye molecule. (b) The structural formula for berberine molecule.

and they have been also verified from the results of X-ray and optical anisotropic techniques [12,13].

Experimental

Mixtures of 25 different concentrations of alizarin dye in berberine were prepared, and they were mixed thoroughly. The structural formulae for these compounds are shown in Figs. 1(a) and (b).The mixtures werekept in desiccators for six hours. Samples were subjected to several cycles of heating, stirring, and centrifuging to ensure homogeneity. Phase transition temperatures of the mixture were measured with the help of a polarizing microscope in conjunction with a hot stage. The samples were sandwiched between the slide and cover slip and were sealed for microscopic observations. Differential scanning calorimetry thermograms were taken for mixture of all 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 at various temperatures for different liquid crystalline phases. Electrical conductivity measurements of the given mixture at different temperatures were carried out using digital LCR meter and a proportional temperature control unit.

Optical Studies

The molecular orientation of optical textures exhibited by the samples was observed and recorded using Leitz polarizing microscope and specially constructed hot stage. The specimen was taken in the form of thin film and sandwiched between slide and cover glass. All concentrations of dye, berberine molecules have a strong tendency to stack into aggregates. A larger number of molecular aggregates produce a polydisperse system [14,15] that can arrange themselves into ordered coexistent biphasic region of chromonic liquid crystalline phases as a function of concentrations and temperature of the given mixture. Biphasic region of chromonic liquid crystals such as N + I, C + I, and N + C phases is still not understood to the same extent as amphiphile-based lyotropic liquid crystals. Lydon has summarized the current state of knowledge on chromonics in two excellent reviews [16,17]. Note that,

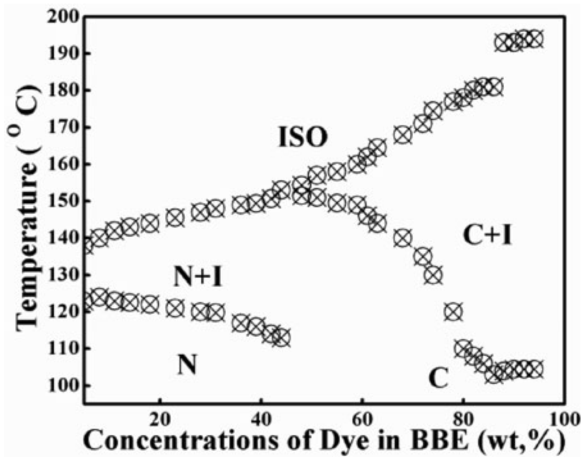

Figure 2. Partial phase diagram for the mixture of alizarin dye in berberine molecule.

chromonic molecules do not show a clear separation of hydrophilic and hydrophobic parts since the hydrophilic groups that impart water solubility are distributed all around the periphery of the hydrophobic aromatic rings. Consequently, chromonic molecules do not form micelles, nor do they show any appreciable surface activity. However, in the presence of alizarin dye, the berberine molecules tend to aggregate into stacks due to both weak Van der Waals interactions between the cores and the hydrophobic effect. All concentrations of dye, if there observed a degree of molecular orientation, as the concentration of dye increases, the molecular aggregated size increases. If the dye concentrations are high enough, the mechanism of molecular aggregated size in lyotropic chromonic liquid crystal is analogous to the worm-like micelles formed by surfactant molecules in solutions. The aggregated size grows definitely, if the entropy increases when the number of aggregates decreases. The stability of these phases depends on both temperature and concentration. Figure 2 shows the phase diagram and typical texture of alizarin dye and berberine mixture. The phase diagram shows very interesting calamitic thermotropic nematic (N) phase and the aggregation of columnar smectic phase (C) and also with co-existent biphasic regions of nematic N + I and aggregated columnar smectic C + I phases respectively at different temperature and at different concentrations of dye molecules.

Mixture of 5% to 44% of alizarin dye is cooled from its isotropic liquid phase, a genesis of nucleation starts in the form of molecular orientations, which grow and segregate the molecules, which identified as co-existent biphasic region of nematic N + I phase and the texture as shown in Fig. 3(a). On further cooling, N + I phase changes over to calamitic thermotropic nematic (N) phase and this phase produces a schlieren texture with disclinations (characterized by two dark brushes of extinction) and point defects-boojums (with four brushes of extinction) [18].

Above 48% of alizarin dye, the binary mixture exhibits a co-existent biphasic region of aggregated columnar smectic C + I phase as shown in Fig. 3(b). In this phase, molecules are stack to form long columnar aggregates which align parallel to each other. There is long-range positional order among the oriented molecules. On further cooling at different temperatures, co-existent biphasic region of columnar smectic C + I phase slowly changes over to aggregation of columnar smectic phase (C) respectively. Due to exhibition of this behavior, chromonic liquid crystals hold great promise to applications as optical materials

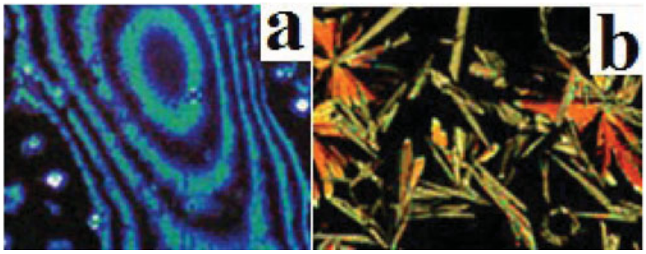

Figure 3. Microphotographs obtained in between the crossed polars. (a) Co-existent biphasic region of nematic (N + I) phase (250X). (b) Co-existent biphasic region of columnar smectic (C + I) phase (250X).

and devices [19–30]. Here it is pertinent to remark that low concentrations of dye with berberine molecule exhibits N + I phase and high concentrations of dye with berberine molecule show C + I phases. This type of behavior observed only in chromonic liquid crystal system [31]. For samples having the concentration of alizarin dye above 44% and below 48%, the optical textures are not clear. In this region, the sample shows viscous nature.

Optical Anisotropy

Results of this investigation are further supported by the optical studies. The refractive indices for extraordinary ray (n_e) and ordinary ray (n_o) of the mixture were measured at different temperatures for different concentrations using Abbe Refractometer and precession Goniometer spectrometer. The temperature variations of refractive indices for the mixtures of 51% of alizarin dye in berberine molecule as shown in Fig. 4. The values of electrical susceptibility for 51% of alizarin dye in berberine molecule have been calculated using Neugebauer relation [32] at different temperatures. The temperature variations of electrical susceptibility for the mixture are as shown in Fig. 5. The figure clearly illustrates

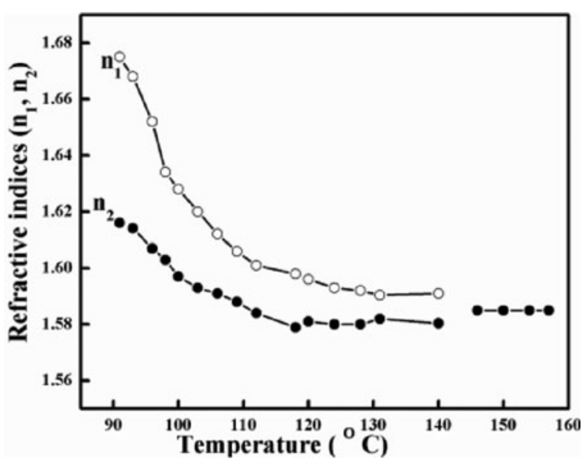

Figure 4. Temperature variations of refractive indices for the mixture of 51% alizarin dye in berberine molecule.

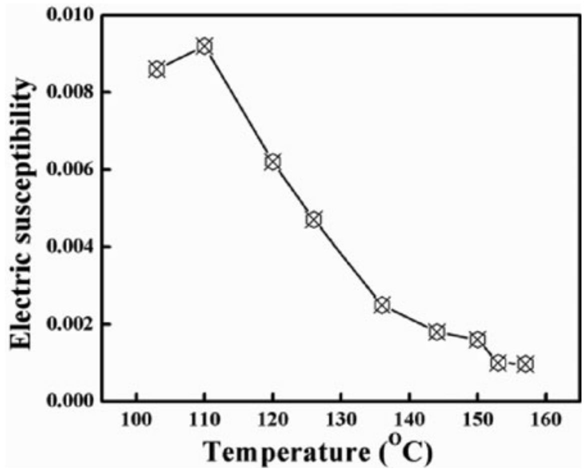

Figure 5. Temperature variations of electrical susceptibility for the mixture of 51% of alizarin dye in berberine molecule.

that wherever there is an isotropic-liquid crystalline phase transition, the value of electrical susceptibility changes appreciably, which indicates that each changes corresponds to occurrence of different liquid crystalline phases. Further, with increase in the concentration of alizarin dye, the value of electrical susceptibility decreases with temperature, because the effective optical anisotropy associated with the molecules of alizarin dye decreases.

Conductivity Measurements

To obtain reliable data on the phase behavior with temperature, electrical-conductivity measurements are necessary. A change in the electrical conductivity with temperature relates to the phase behavior of lyotropic, thermotropic, and chromonic liquid crystalline systems [33]. The temperature variations of electrical conductivity are shown in Fig. 6, which clearly illustrates that there is some change in the value of electrical conductivity from 103°C to 157°C, while cooling from isotropic phase for the mixture of 51% alizarin dye. For the mixture of 51% alizarin dye, the sequence of phase changes from co-existent biphasic region of aggregated columnar smectic C + I phase to aggregation of columnar smectic phases (C) phase. Here it has been found that the electrical conductivity goes on increasing as the temperature decreases. This suggests that aggregated molecular size start to grow toward decreasing the temperature and then the system becomes more orderly [34,35].

X-Ray Studies

The X-ray diffractometer traces obtained for the mixture of 31% of alizarin dye at temperatures 110°C and 130°C are shown in Fig. 7(a), the diffraction peaks at these temperatures correspond to calamitic thermotropic nematic (N) phase and the co-existent biphasic region of nematic N + I phase respectively by using JEOL diffractometer with the settings: TC4, CPS400, channel width 100 for $\lambda = 1.934$ Å. X-ray diffraction method appears to be the only practical and reliable way to find the crystalline size measurement [36–38] of the different liquid crystalline materials. Similarly the X-ray traces obtained for the

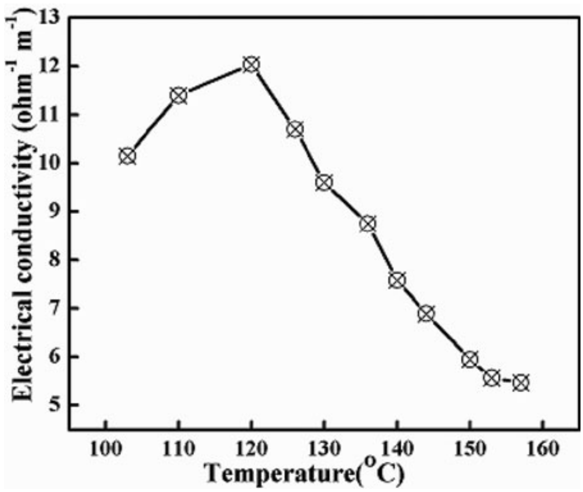

Figure 6. Temperature variation of electrical-conductivity σ (Ω^{-1} m^{-1}) for the sample of 51% of alizarin dye in berberine molecule.

mixture of 63% of alizarin dye at temperatures 110°C and 150°C as shown in Fig. 7(b), the diffraction peaks at these temperatures corresponds to co-existent biphasic region of aggregated columnar smectic C + I and columnar smectic (C) phases respectively. Perfect liquid crystals would extend in all directions to infinity, so we can say that no crystal is

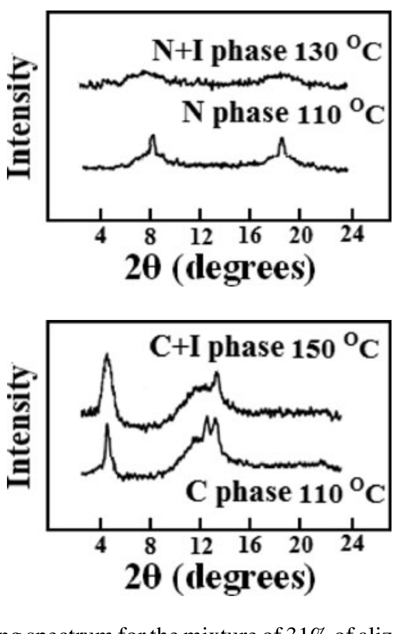

Figure 7. (a) X-ray broadening spectrum for the mixture of 31% of alizarin dye in berberine molecule at different temperature of N + I and N phases. (b) X-ray broadening spectrum for the mixture of 63% alizarin dye in berberine molecule at different temperature of C + I and C phases.

perfect due to its finite size. The deviation from perfect liquid crystallinity leads to a broadening of the diffraction peaks. In order to estimate the crystalline size of materials from the corresponding broadening X-ray diffraction peaks by using 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. The phase transition temperatures increases as it moves from crystalline phase to amorphous region [39,40], which clearly illustrates that, the crystalline size of the liquid crystalline materials decrease with increasing the temperature. Here in Fig. 7(a), the coexistent biphasic region of nematic N + I phase is energetically not stable, because the molecular ordering of this phase not clear. Hence it is very difficult to identify the intensity of peak in N + I phase. The calamitic thermotropic nematic N phase is energetically stable and hence it shows the intensity of two small peaks. The crystalline size of the respective nematic N phase is 38.5018 nm.

From Fig. 7(b), co-existent biphasic region of aggregated columnar smectic C + I phase is energetically stable, molecular ordering of this phase shows the intensity of two peaks. The crystalline size of C + I phase comes out to be 43.5213 nm and aggregation of columnar smectic phases (C) phase is more stable for large crystallites of 49.7529 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 crystalline size of the liquid crystalline materials are big enough to indicate that the molecular ordering [41] of layer structure increases as well as decrease the temperature.

Conclusions

Optical microscopic investigations of binary mixture of dye and berberine molecule clearly show the molecular ordering of co-existent biphasic regions of nematic N + I and aggregated columnar smectic C + I phases for lower and higher concentrations of binary mixture of alizarin dye and berberine molecule respectively at different temperatures. Changes in the values of electrical conductivity with temperature suggest that the size of aggregated molecules goes on increasing and the electrical conductivity is also increasing, while the mixture is cooled from the isotropic phase. X-ray studies lend support to find the grain size of the liquid crystalline phases at respective temperature.

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