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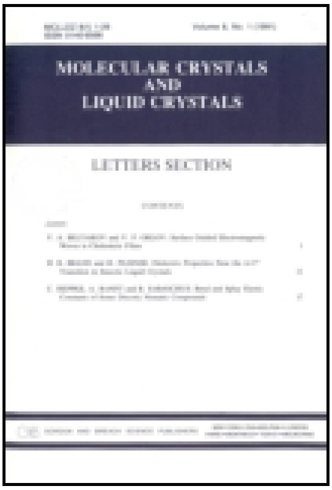

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Optical Characterization of Lyotropic Chromonic Liquid Crystals

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Optical Characterization of Lyotropic Chromonic Liquid Crystals

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We report the results of our studies on the optical and thermal properties of binary mixture of compounds, viz., Berberine (BBE) and Poly-ethylene glycol (PEG). The mixture shows very interesting coexistent biphasic regions N + I and N + C phases respectively at different concentrations of BBE sequentially when the specimen is cooled from its isotropic liquid phase. The temperature variations of optical anisotropy and optical textures have also been discussed. Formation of above molecular orientations has been confirmed by X-ray studies.

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

Introduction

The mesogenic liquid crystals have to be anisometric (non-spherical) objects in order to allow for the essential long-range orientational order. As an example, colloidal particle in aqueous suspensions can exhibit long-range orientational order, usually forming achiral phases [1]. Even bio-molecules like tobacco mosaic virus with its long rod like shape are suited for lyotropic liquid crystalline structure [2]. In solution of amphiphilic as well as certain aromatic matter (e.g., dyestuffs), aggregates of monomer can form; different anisometric shapes can be developed and thus the aggregates take the role of the building blocks of lyotropic liquid crystals. A remarkable example of nonmicellar chiral system based on an achiral host phase of column-like aggregates of large, disc-like molecules has been published by Usol' tseva, et al. [3].

In recent years, the existence of a second class of aqueous lyotropic mesophases, termed chromonic liquid crystals, has come to be better recognized and understood [4–6]. Unlike typical lyotropic phases formed by amphiphilic molecules having a hydrophilic head and a hydrophobic tail, chromonic liquid crystals are formed by water-soluble molecules that contain planar aromatic rings. Examples of chromonic liquid crystal-forming molecules include drugs, dyes, and nucleic acids [7, 8].

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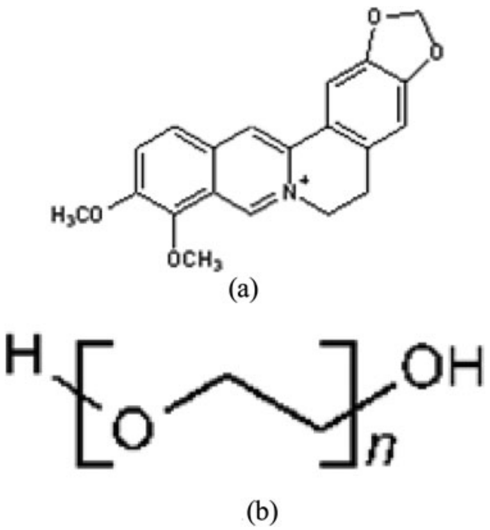

Figure 1. (a) Structural formula of the berberine (BBE) molecules. (b) Structural formula of the polyethylene glycol (PEG) molecules.

In the presence of berberine, the molecules tend to aggregate into stacks due to both weak Van der Waals interactions between the cores and the hydrophobic effect. At all concentrations, there is some degree of aggregation. As the concentration increases, the distribution of aggregate size shifts to higher and higher numbers of molecules in the aggregates. If the concentration is high enough to form large and interacting rod-like aggregates, liquid crystalline phases are formed. The stability of these phases depends on both temperature and concentration.

Some of the investigators sought to synthesize new molecules [9] and study the fundamental properties such as the fluctuations associated with the liquid crystal to isotropic liquid phase transitions [10]. This was followed by work on optical, thermal, microscopic studies, and X-ray measurements of the chromonic liquid crystals [11–14].

In the present investigation, we have shown the coexistent biphasic regions N + I and N + C phases for all concentrations in binary mixture of Berberine (BBE) and Polyethylene glycol (PEG) with water as the solvent. We have discussed the results of X-ray diffraction studies of nematic phase, columnar phase, and coexistent biphasic regions N + C phases respectively at different temperatures. Optical anisotropy and optical texture studies have been carried out for the molecular aggregation of the phases at different temperatures. In light of the investigations, an attempt has been made to understand the coupling between aggregate structure and the mesophase order looking into the observations regarding lyotropic chromonic liquid crystals [15], where-in it has been observed that, the aggregates formed for all concentrations of the given mixture are large enough to align, and there by aggregate size increases into supramolecular assemblies.

Experimental

The structural formulae for BBE and PEG molecules are as shown in Figures 1(a, b). Mixtures of 25 different weight percent concentrations of BBE in PEG were prepared taking

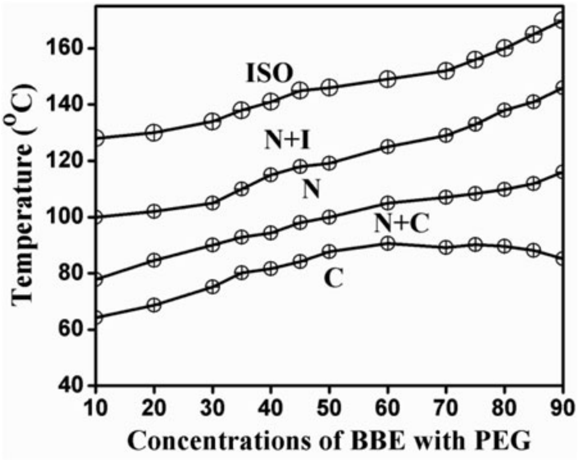

Figure 2. Partial phase diagram for the mixtures of BBE in PEG.

water as the solvent and they were mixed thoroughly. These mixtures were kept in desiccators for 6 hr. Samples were subjected to several cycles of heating, stirring and centrifuging to ensure homogeneity. Phase transition temperatures of these mixtures 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. DSC thermograms were taken for mixtures 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 orientations of 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. Even in the dilute isotropic (I) solutions, chromonic molecules have a strong tendency to stack into aggregates. A larger number of aggregates produce a polydisperse system of linear aggregates [16, 17] that can arrange themselves into ordered chromonic liquid crystalline phases as a function of concentration and temperature. Figure 2 shows the phase diagram and typical textures of BBE and PEG mixture. The phase diagram shows very interesting nematic (N) and columnar (C) phases and also with the broad coexistent regions N + I and N + C respectively at different temperatures.

Mixture with 50% of BBE is cooled from its isotropic liquid phase, a genesis of nucleation starts in the form of molecular orientations, which is growing and segregates the molecules, which are identified as the broad coexistent nematic biphase N + I and the texture is as shown in Figure 3(a). On further cooling, N + I phase changes over to N phase. The N phase produces schlieren textures with disclinations (characterized by two dark brushes of extinction) and point defects-boojums (with four brushes of extinction) as

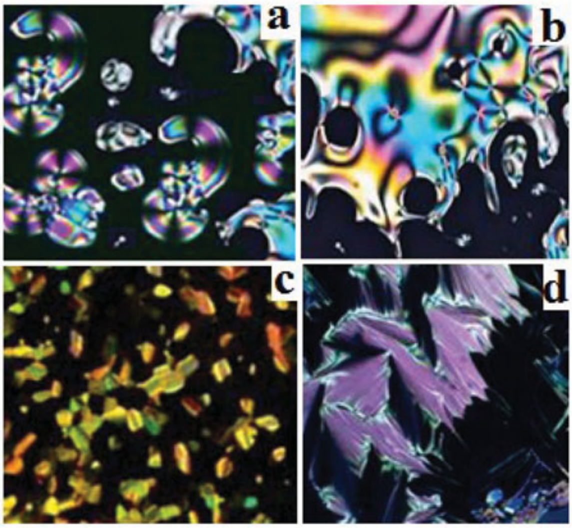

Figure 3. Microphotographs obtained in between the crossed polars. (a) With broad coexistent nematic biphase N + I phase (250×). (b) Schlieren texture of Nematic (N) phase (250×). (c) With broad coexistent biphasic regions N + C phases (250×). (d) Aggregation of columnar (C) phase (250×).

shown in Figure 3(b) [18]. In N phase, molecules stack to form long columnar aggregates which align parallel to each other. There is no long-range positional order among the columns. On further cooling the specimen, the schlieren texture of nematic phase slowly changes over to another broad coexistent biphasic region N and C phases, which is the characteristics of N + C phase as shown in Figure 3(c). On further cooling, the columnar phase shows characteristic "developable" domains [18] as shown in Figure 3(d). Due to exhibition of this behavior, Chromonic liquid crystals hold great promise to applications as optical materials and devices [19–30].

Optical Anisotropy

Results of this investigation are further supported by the optical studies. The refractive indices for extraordinary ray (ne) and ordinary ray (no) 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 50% of BBE in PEG are as shown in Figure 4. The value of ne is greater than no, indicating that the material is uniaxial positive. The values of electrical susceptibility for 50% of BBE in PEG have been calculated using Neugebauer relation [31] at different temperatures. The temperature variations of electrical susceptibility for the mixture are as shown in Figure 5. From the figure, it can be observed that wherever there is an isotropic-liquid crystalline phase transition, the value of electrical susceptibility changes appreciably, which indicates that each change corresponds to the occurrence of different chromonic liquid crystalline phases. Further, with increase in the concentration of BBE, the value of electrical susceptibility decreases with temperature, because the effective optical anisotropy associated with the molecules of BBE also decreases.

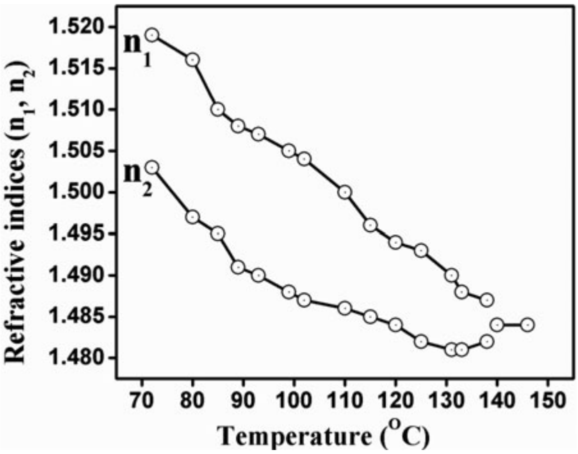

Figure 4. Temperature variations of refractive indices for the mixture of 50% BBE in PEG.

Conductivity Measurements

To obtain reliable data on the phase behavior with temperature, electrical-conductivity measurements are necessary. An abrupt increase or decrease of electrical-conductivity with temperature relates to the phase behavior of lyotropic systems [32]. A temperature variation of electrical-conductivity is shown in Figure 6. The figure clearly illustrates that there is change in the value of electrical conductivity up to 80°C, while cooling from isotropic phase for the mixture of 50% BBE. With further decrease in temperature, the electrical conductivity starts decreasing as we move towards the room temperature. In the mixture having 50 weight % of BBE, we observe sequential change of phase from N + I to N, N to N + C, and N + C to C. We observe that there is some immediate appreciable change in the value of electrical conductivity at these phase changes. The change is observed only after further cooling. This suggests that, the size of aggregates starts growing toward decreasing phase transition temperature and the system moves towards more orderliness.

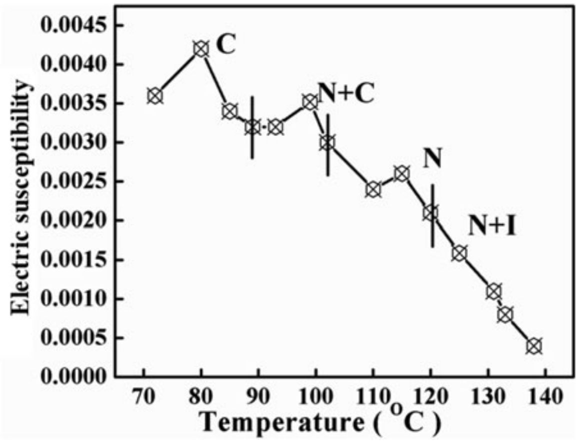

Figure 5. Temperature variations of electrical susceptibility for the mixture of 50% BBE in PEG.

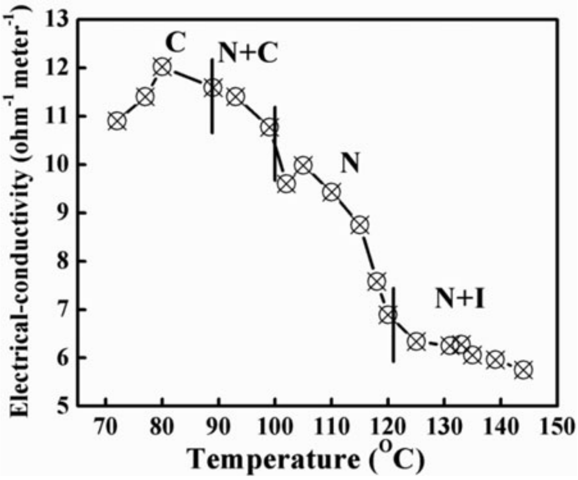

Figure 6. Temperature variation of electrical-conductivity σ (Ω-1 m-1) for the sample of 50% BBE in PEG.

Finally, below 80°C size of aggregates becomes so large that the specimen starts moving toward the crystalline nature [33, 34].

X-Ray Studies

The X-ray diffractometer traces obtained for the mixture of 50% of BBE at temperature 75°C, 95°C, and 110°C are as shown in the Figure 7. The diffraction peaks at these temperatures correspond to N, N + C and C phases respectively, using JEOL diffractometer with the settings: TC4, CPS400, channel width 100 for λ = 1.934 Å. XRD method appears to be only practical and reliable way to find the crystalline size measurement [35–37] of the

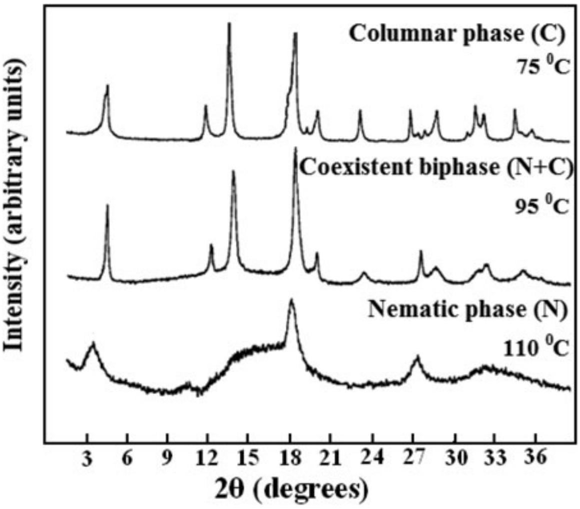

Figure 7. XRD traces obtained for the mixture of 50% BBE in PEG.

liquid crystalline materials. Perfect liquid crystals would extend in all directions to infinity, so we can say that no crystal is perfect due to its finite size. The deviation from perfect liquid crystallinity leads to broadening of the diffraction peaks. Estimation of the crystallite size from the broadening of the corresponding X-ray diffraction peaks has been done by using Scherer'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. As the temperature increases, the specimen moves from crystalline phase to amorphous phase [38, 39], which clearly illustrates that, the crystallite size of the material decreases with increasing the temperature. Because, N phase is more stable energetically for small crystallite size (30.0377 nm), but the N + C (58.9048 nm) and C (59.9043 nm) phases are more stable for large crystallite size. N phase transforms into N + C and C phases, respectively, when the crystalline size of the liquid crystalline materials are big enough to indicate that the molecular ordering [40] of layer structure increases as the temperature of the mixture decreases.

Conclusions

Microscopic investigation of the binary mixture of BBE and PEG shows the molecular orientation of coexistent biphases N + I and N + C for all concentrations of BBE molecule respectively at different temperatures. The observation from the various studies of this unconventional sequence clearly indicates that the mixture is exhibiting the lyotropic chromonic liquid crystalline nature. Changes in the value of electrical-conductivity with the variation of temperature suggest that as the mixture is cooled from the isotropic phase, the size of aggregates goes on increasing and the electrical conductivity also goes on increasing. But below a particular temperature, the size of aggregates becomes so large that the specimen moves towards crystalline nature. X-ray studies are lending support to the grain size of the different liquid crystalline phases.

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