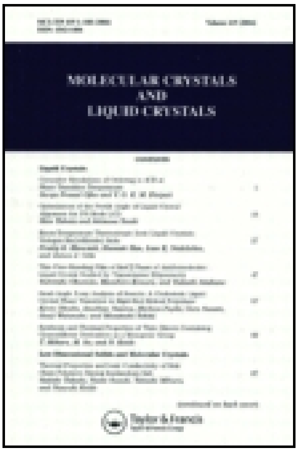

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Mesophase Formation in Binary Mixtures of Berberine and Glacial Acetic Acid

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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 Glacial acetic acid (GAA). The mixture shows very interesting coexistent nematic biphase (N+I) and nematic phase for different concentrations of BBE sequentially when the specimen is cooled from its isotropic phase. The order parameter (S) of the coexistent nematic biphase is estimated with the help of optical anisotropy from the measured refractive index and density data. The temperature variation curve of experimentally found order parameter is well fitted with the Maier–Saupe theoretical curve. The temperature variation of electrical conductivity is also discussed. Formation of above molecular orientations has been confirmed by optical studies.

Keywords Binary mixture; lyotropic chromonic; molecular aggregation; nematic; order parameter

Introduction

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 [1–3]. 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 [4,5].

Berberine (BBE), which is considered to be an antibiotic [6,7] has been widely studied. When applied in vitro and in combination with methoxyhydnocarpin, an inhibitor of multidrug resistance pumps, BBE inhibits growth of Staphylococcus aureus [8] and Microcystis aeruginosa [9], a toxic cyanobacterium. BBE is a component of some eye drop formulations. There is some evidence that it is useful in the treatment of trachoma [10], and it has been a standard treatment for leishmaniasis [11]. BBE lowers elevated blood total cholesterol, LDL cholesterol, triglycerides, and atherogenic apolipoproteins [12,13]. The structure of BBE is presented in Fig. 1.

Chromonic liquid crystals are still not understood to the same extent as amphiphile-based lyotropic liquid crystals. Lydon has summarized the current state of knowledge

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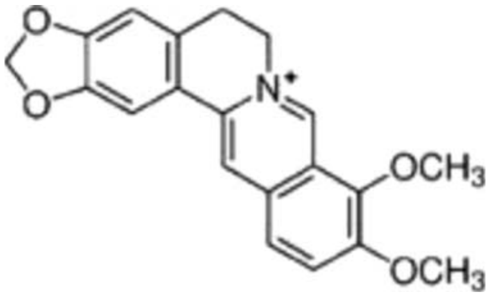

Figure 1. Molecular structure of BBE.

on chromonics in two excellent reviews [3,4]. Note that chromonic molecules do not show a clear separation of hydrophilic and hydrophobic parts since the hydrophilic (ionic or hydrogen-bonding) 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 BBE, 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 recent investigations sought to synthesize new molecules [15] or study fundamental properties such as the fluctuations associated with the liquid crystal to isotropic liquid transitions [16]. This was followed by work on the oriented monolayers that could be formed with these materials [17] and the phase changes induced by adding solvent to the solution [18]. Investigations utilizing both optical and X-ray measurements on aligned liquid crystal samples [19] have been done to look at the chromonic type of liquid crystals. There have been reports of worm-like micellar formation in a chromonic liquid crystal [20]. X-ray microscopy study of the textures in the dried films formed by chromonic liquid crystal systems [21] and an effort to immobilize the chromonic liquid crystal structure with a sol-gel process have also been performed by few investigators.

In the present investigation, we have shown the coexistent nematic biphase [Nematic + Isotropic (N+I)] and Nematic (N) phases respectively at different concentrations in the binary mixture of BBE and Glacial acetic acid (GAA). Birefringence and optical texture studies have been carried out for the molecular aggregation of the above phases at higher temperatures. In light of the above investigations, an attempt has been made to understand the coupling between aggregate structure and the mesophase order in light of the observations regarding lyotropic chromonic liquid crystals [22], wherein it has been observed that the aggregates formed at low concentrations are not large enough to align, and at larger concentrations aggregate size increases into supramolecular assemblies.

Experimental

Mixtures of 25 different concentrations of BBE in GAA were prepared and were mixed thoroughly. These mixtures of concentrations were kept in desiccators for 6 h. 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

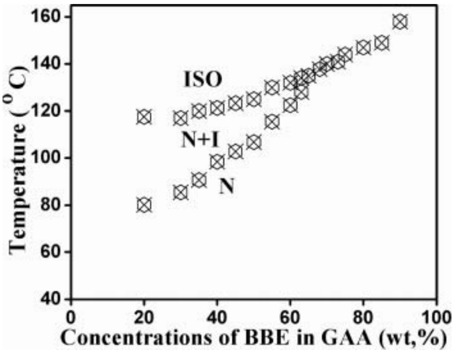

Figure 2. Partial phase diagram for the mixture of BBE and GAA.

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 (DSC) thermograms were taken for mixtures of all concentrations using the Perkin-Elmer DSC II Instrument facility available at Raman Research Institute, Bangalore, India. Electrical conductivity measurements of the given mixture at different temperatures were carried out using digital LCR meter and a proportional temperature control unit.

Phase Diagram

The partial phase diagram, shown in Fig. 2, is drawn considering the phase transition temperatures against the concentrations of the given mixture, which clearly illustrates the presence of BBE in GAA. This partial phase diagram exhibits a very interesting Nematic (N) and coexistent nematic biphase, i.e., Nematic + Isotropic (N+I) biphase, which is the characteristic of chromonic liquid crystalline phases at different temperatures. In our experimental studies the coexistent nematic biphase (N+I) and phase N have been identified on the basis of microscopic texture.

These observations indicate that the present mixture exhibits lyotropic chromonic liquid crystalline nature [22]. For lower concentrations and higher temperatures, some aggregates are not showing the preferred direction for alignment and others remain randomly oriented. At this stage, in this region with up to 20% of concentration of BBE in GAA, the molecular orientations are not clear to show any of the liquid crystalline phases. The aggregates are getting aligned and showing N+I and N phases ranging from the concentrations of 20% to 90% of BBE in GAA at different temperatures.

Optical Texture 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 slide and cover glass. The molecular aggregates are not clear up to 20% concentration of BBE in GAA. The N+I and N phases are clear above 20% of BBE. The concentration of BBE ranging from 20% to 90% has been considered for the discussion. As the concentration of BBE increases, the molecular aggregates are aligned along a particular direction, and hence exhibit a coexistent nematic biphase at higher temperatures. When the specimen of 50%

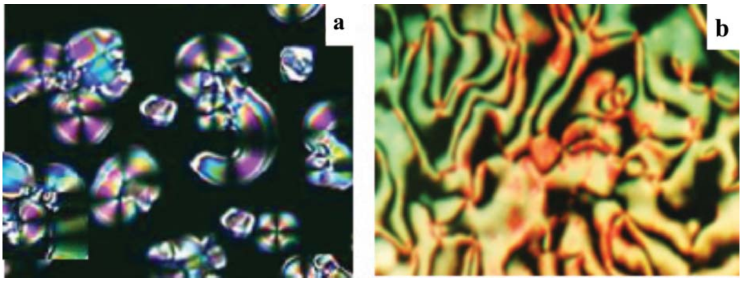

Figure 3. Microphotographs showing (a) coexistent nematic biphase (N+I) (180×), (b) Schlieren texture of nematic phase (N) (180×).

BBE is cooled from its isotropic liquid phase, it exhibits I – N+I – N phases sequentially. When the sample is cooled from isotropic liquid phase, the genesis of nucleation starts in the form of molecular orientations, which grows and segregates the molecules that are identified as the existence of nematic biphase N+I, and the texture is as shown in Fig. 3(a). On further cooling, N+I biphase 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 shown in Fig. 3(b), and it remains as such toward room temperature. Here it is pertinent to remark that the molecular aggregation increases at low temperature and different concentrations of BBE. In the N phase, the molecules stack to form long columnar aggregates, which align parallel to each other. There is no long-range positional order in columns. Here it is very interesting to note that the coexistence of N+I biphases decreases with increasing BBE concentrations, whereas with increase in BBE concentration, N phase increases.

Because of the exhibition of this behavior, chromonic liquid crystals hold great promise toward applications as optical materials and devices in high technology. Potential applications reported for chromonic liquid crystals include biosensors [23–25], polarizing films [26–30], optical retardation plates [31,32], and micro-patterned polarizing elements for stereoscopic displays [33,34].

Birefringence Studies

The molecular orientations of coexistent nematic biphase in lyotropic system are generally formed by amphiphilic aggregation with bilayer structure [35]. As in nematic phase of thermotropic system, the bilayer amphiphilic aggregations show some degree of parallel orientation, which is responsible for the macroscopic anisotropy of the phase. The birefringence study helps us to understand the optical anisotropic properties of samples. The orientational order parameter (S) of the coexistent nematic biphase is essential to understand the degree of orientations of molecular aggregation [36].

In the present investigation we have measured the temperature variation of refractive indices (n_1 and n_2) and densities for mixture with different concentrations by using Abbe refractometer and precision Goniometer spectrometer at the wavelength 5893 Å in the coexistent nematic biphase. Refractive indices n_1, due to extraordinary ray, and n_2, due to ordinary ray, have been determined. Saupe used the modified Lorentz–Lorentz [37] formula for the calculation of orientational order parameters of lyotropic mixture. The refractive indices n_1 and n_2 are given by

$$\frac{n_1^2-1}{n_2^2+2}=4\frac{\pi}{3N}\left[W_{\mathrm{GAA}}\alpha_{\mathrm{GAA}}+W_{\mathrm{BBE}}\alpha_{\mathrm{BBE}}-\left(\frac{2}{3}\right)W_{\mathrm{BBE}}\Delta\alpha_{\mathrm{BBE}}S\right], \tag{1}$$

$$\frac{n_1^2-1}{n_2^2+2}=4\frac{\pi}{3N}\left[W_{\mathrm{GAA}}\alpha_{\mathrm{GAA}}+W_{\mathrm{BBE}}\alpha_{\mathrm{BBE}}-\left(\frac{1}{3}\right)W_{\mathrm{BBE}}\Delta\alpha_{\mathrm{BBE}}S\right], \tag{2}$$

where N is the number of molecules per unit volume of the mixtures, W_{GAA} and W_{BBE} are the mole fractions of GAA and BBE respectively, and α is the mean polarizability of the respective compounds. For the estimation of S of the coexistent nematic biphase, we assume only the birefringence Δn of BBE molecules [35]. As the polarizability tensor of BBE can be approximated with principal polarizability, α_1 is parallel to the long axis of the molecule and α_2 is perpendicular to it. The optical anisotropy $(\Delta\alpha)$ contribution from acetic acid is neglected because the concentration of BBE molecules is increased. Therefore, only $\Delta\alpha$ of BBE molecules is considered, $\Delta\alpha = \alpha_1 - \alpha_2$ and $S = 1/2[3\cos^2\theta - 1]$ is the degree of order of BBE molecules, where θ is the angle between the long molecular axis and optic axis of molecular aggregation in the coexistent nematic biphase and $\cos^2\theta$ is the average over molecular orientation.

From Eqs. (1) and (2), and using $\Delta n = (n_e - n_o) \ll 1$, we obtain

$$\Delta n=\frac{\left[2\pi(n_2^2+2)^2N\Delta\alpha W_{\mathrm{BBE}}S\right]}{9n_2}. \tag{3}$$

In order to estimate the value of optical anisotropy $(\Delta\alpha)$ of BBE molecules, the values of $(\alpha_{||})_{\mathrm{eff}}$, i.e., the polarizability along the axis of molecules, and $(\alpha_{\perp})_{\mathrm{eff}}$, the polarizability perpendicular to the long axis of molecules, are calculated. The value of $(\alpha_{||})_{\mathrm{eff}}$ for each molecule is calculated from the optical anisotropy of bond polarizability data for the wavelength of 5893 Å [38] assuming that all molecules have trans-configuration, and hence $(\alpha_{\perp})_{\mathrm{eff}}$ may also be calculated. Using the values of $(\alpha_{||})_{\mathrm{eff}}$, $(\alpha_{\perp})_{\mathrm{eff}}$, and α, the mean polarizability, the value of $\Delta\alpha$ is estimated [39]. The value of $(\Delta\alpha)$ for BBE molecules turns out to be 5.13×10^{-24} cm^3. The order parameter of the coexistent nematic biphase is calculated with the help of $(\Delta\alpha)$ value. The value of S of the mixture was estimated for different concentrations at different temperatures. Boden et al. [40] have pointed out in their study that the variation of birefringence with temperature is dependent upon both size and shape of molecular aggregation, in addition to their dependence on orientational order. However, we also noted that value of S varies with mole percentage of BBE in coexistent nematic biphase and it is observed that S decreases with decrease in the concentration of BBE. The temperature variations of S of the coexistent nematic biphase are shown in Fig. 4, and the experimental values of order parameters are compared with the Maier–Saupe theoretical curve. It is observed that variation in S values agrees well with the Maier–Saupe theoretical curve. The values of birefringence are in good agreement with the values measured using the interference techniques [41,42].

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 [43]. The temperature

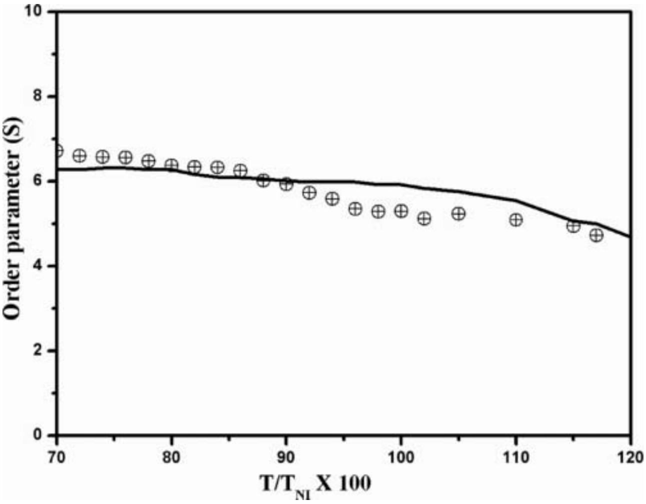

Figure 4. Temperature variation of order parameters of coexistent nematic biphase.

variation of electrical conductivity in the present case is as shown in Fig. 5. As it can be seen from Fig. 5, there is not much change in the value of electrical conductivity up to 75°C during cooling from the isotropic phase in case of the mixture with 50% concentration of BBE. With further decrease in temperature, the electrical conductivity goes on increasing up to 60°C, and below this the electrical conductivity starts decreasing as we move toward room temperature.

Thus, for the mixture with 50% concentration of BBE, though there is a change of phase from N+I to N, there is no immediate appreciable change in the value of electrical conductivity. The change is observed only after further cooling. This suggests that the size of aggregates starts growing below 75°C and the system moves toward more orderliness.

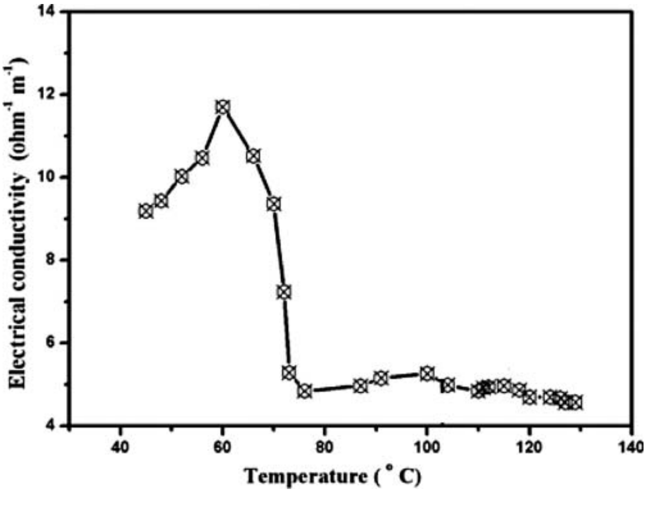

Figure 5. Temperature variation of electrical conductivity σ (Ω^{-1} m^{-1}) for the sample of 50% of BBE in GAA.

Finally, below 60°C, size of aggregates becomes so large that the specimen starts moving toward crystalline nature.

Conclusions

Microscopic investigation of the binary mixture of BBE and GAA shows the molecular orientation of coexistent nematic biphase for different concentrations of BBE molecule at different temperatures. Observations from different studies of this unconventional sequence clearly indicate that the mixture is exhibiting the lyotropic chromonic liquid crystalline nature. The birefringence study shows that the contribution of birefringence of the mixture is mainly due to BBE. Changes in the value of electrical conductivity with variation of temperature suggest that as the mixture is cooled from the isotropic phase, the size of aggregates increases as also the electrical conductivity. But below a particular temperature, the size of aggregates becomes so large that the specimen moves toward crystalline nature. It is observed that the variation of order parameter values is in good agreement with the Maier–Saupe theoretical curve.

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