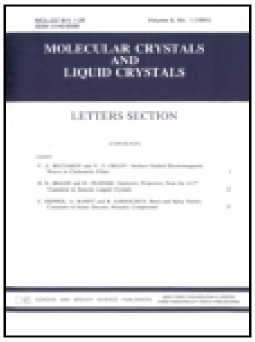

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Aggregated Columnar Biphasic Region of Lyotropic Chromonic Liquid Crystalline Phase

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We report the results of our studies on the optical and thermal properties of binary mixture of compounds viz., abietic acid and ethylene glycol. The mixture shows very interesting co-existent biphasic region of aggregated columnar (C+I) and columnar (C) phases respectively at different concentrations of abietic acid sequentially when the specimen is cooled from its isotropic liquid phase. The temperature variations of optical anisotropy and optical textures have also been discussed.

Keywords: Biphasic region; lyotropic chromonic; molecular aggregation; nematic; optical anisotropy

Introduction

In recent years, the existence of a second class of aqueous lyotropic mesophases, termed chromonic liquid crystals, has been 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].

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 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 groups that impart water solubility are distributed all around the periphery of the hydrophobic aromatic rings. Consequently, the chromonic molecules do not form micelles, nor do they show any appreciable surface activity. However, in presence of abietic acid, the molecules tend

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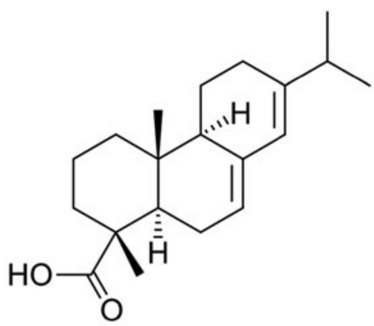
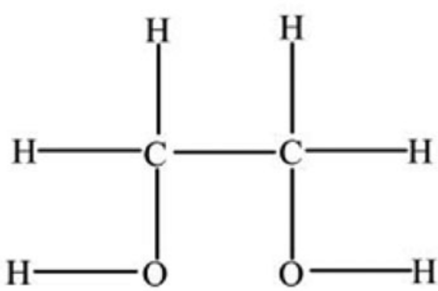
to aggregate into stacks due to both weak Van der Waals interactions between the cores and the hydrophobic effect. At all concentrations, there is some degree of aggregation. As the concentration increases, the distribution of aggregated size shifts to higher and higher numbers of molecules in the aggregates. 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 concentrations.

Some recent investigations sought to synthesize new molecules [6] or study fundamental properties such as the fluctuations associated with the liquid crystal to isotropic liquid transitions [7]. This was followed by work on the oriented monolayers that could be formed with these materials [8] and the liquid crystalline phase changes by adding solvent to the solution [9]. Investigations utilizing both optical and X-ray measurements on aligned liquid crystal samples [10] 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 [11]. X-ray, microscopic study of the textures in the dried films formed by chromonic liquid crystal systems [12] 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 co-existent biphasic region of aggregated columnar (C+I) and columnar (C) phases respectively at different temperatures and concentrations in binary mixture of abietic acid and ethylene glycol. Birefringence and optical texture studies have been carried out for the molecular orientation of the above phases at higher temperatures. In light of the above investigations, an attempt has been made to



(a)



(b)

Figure 1. (a) Structural formula of the Abietic acid molecule. (b) Structural formula of the ethylene glycol molecule.

understand the coupling between aggregate structure and the mesophases order regarding lyotropic chromonic liquid crystals [13], 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 Studies

In the present study, we have used the materials, namely, abietic acid and ethylene glycol. The structural formulae for abietic acid and ethylene glycol molecules are shown in Figs. 1(a) and 1(b). Mixtures of 25 different concentrations of abietic acid and ethylene glycol were prepared, and they were mixed thoroughly. The mixtures of these concentrations were kept 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. 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. The density and refractive indices of the mixtures were measured at different temperatures employing the technique described in our earlier paper [14]. Electrical conductivity measurements of the given mixture at different temperatures were carried out using digital LCR meter and a proportional temperature control unit.

Theoretical Analysis General Theory on Polarizability

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

$$\vec{D} = \varepsilon_0 \vec{E} + \vec{P}$$

Since

$$\vec{D} = \frac{q}{A} = \frac{\varepsilon_0 \varepsilon_r q}{A \varepsilon_0 \varepsilon_r} = \varepsilon_0 \varepsilon_r \vec{E} = \varepsilon \vec{E}$$

Where

$$\varepsilon = \varepsilon_0 \varepsilon_r$$

Therefore,

$$\begin{aligned}
\varepsilon \vec{E} &= \varepsilon_0 \vec{E} + \vec{P} \\
\vec{P} &= \varepsilon_0 \varepsilon_r \vec{E} - \varepsilon_0 \vec{E} = \varepsilon_0 \vec{E}\,(\varepsilon_r - 1) \\
(\varepsilon_r - 1) &= \frac{\vec{P}}{\varepsilon_0 \vec{E}} =
\end{aligned}$$

where is the electrical susceptibility of the liquid crystalline medium.

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

$$\begin{aligned}
&\vec{\mu_e} \vec{E} \\
&\vec{\mu_e} = \alpha_e \vec{E}
\end{aligned}$$

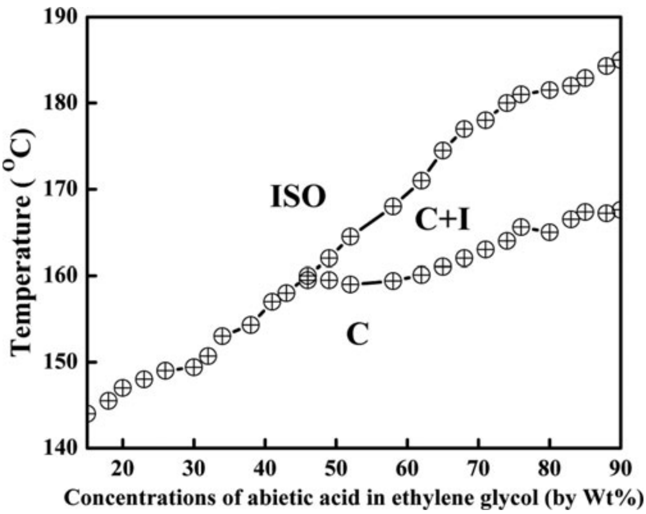


Figure 2. Partial phase diagram for the mixture of abietic acid and ethylene glycol.

where α_e is called electronic polarizability.

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

$$\vec{P}_e = N\overrightarrow{\mu_e} = N\alpha_e\vec{E}$$

where N is the number density of molecules of liquid crystal.
But

$$\vec{P}_e = \varepsilon_0\vec{E}\,(\varepsilon_r - 1)$$

Therefore,

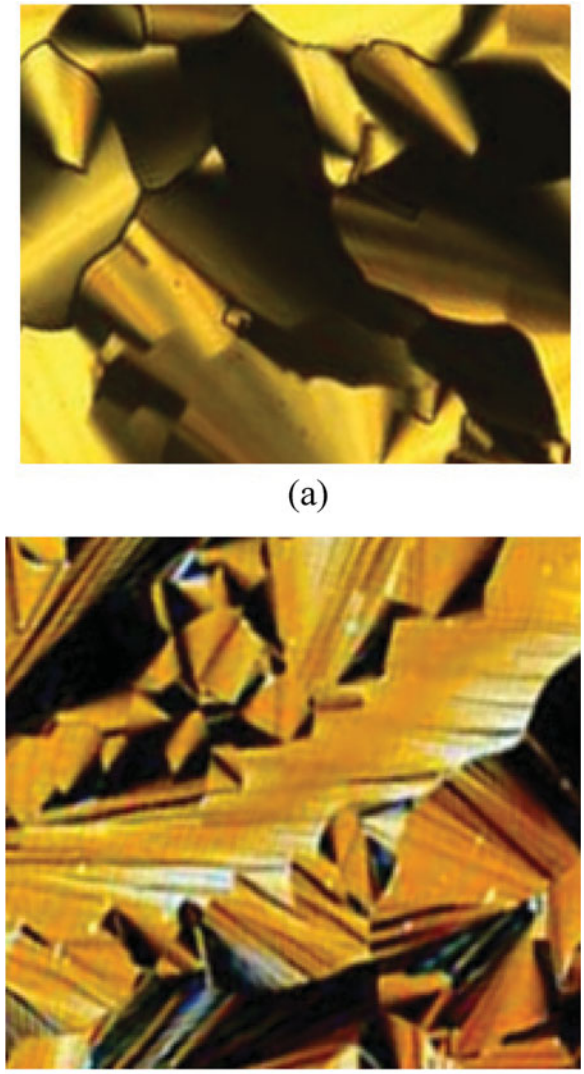
$$\varepsilon_0\vec{E}\,(\varepsilon_r - 1) = N\alpha_e\vec{E}$$

or

$$(\varepsilon_r - 1) = \frac{N\alpha_e}{\varepsilon_0}$$

Results and Discussion Phase Diagram

The partial phase diagram as shown in Fig. 2 is drawn by considering the phase transition temperatures against the concentrations of the given mixture, which clearly illustrates the presence of abietic acid in ethylene glycol. This partial phase diagram exhibits a very interesting columnar (C) and co-existent biphasic region of aggregated columnar (columnar phase + isotropic (C+I)) phase, which is the characteristic of chromonic liquid crystalline phase at different temperatures. In our experimental studies, the co-existent biphasic region of aggregated columnar (C+I) and columnar (C) phases have been identified on the basis of microscopic texture. These observations indicate that, the present mixture exhibits lyotropic chromonic liquid crystalline nature [15].



(a)

(b)

Figure 3. Microphotographs obtained in between the crossed polars, (a) co-existent biphasic region of aggregated columnar C+I phase (250X). (b) Aggregation of columnar (c) phase (250X).

For higher concentrations and higher temperatures, in some region the aggregates are not showing the preferred direction for alignment and others remain randomly oriented. At this stage, in this region with concentrations ranging from 46% to 90% of abietic acid in ethylene glycol, the molecular orientations are not clear to show any of the liquid crystalline phases but shows a biphasic region of chromonic nature. The aggregates are getting aligned and showing C+I and C phases ranging from the concentrations of 15% to 90% of abietic acid in ethylene glycol at different temperatures.

Optical Studies

The molecular orientations of 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 slip.

Mixture with 52% of abietic acid in ethylene glycol 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 co-existent biphasic region of aggregated columnar (C+I) phase and the texture observed is as shown in Fig. 3(a). On further cooling, C+I phase changes over to columnar (C) phase and this phase is as shown in Fig. 3(b).

At low concentrations, there is stability as function of temperature up to 45% of abietic acid in ethylene glycol. A columnar phase is found to be stable at low temperatures in the concentrations ranging from 15% to 90%. With increasing the temperature, at higher concentrations the columnar (C) phase disappears, which moves toward the appearance of co-existent biphasic region of aggregated columnar (C+I) phase.

For most of the phase diagrams, the biphasic region of aggregated columnar (C+I) phase is found to be unstable. However, when aggregation is very weak (high temperature), C+I phase becomes unstable with respect to a liquid crystalline isotropic phase. In addition to the macroscopic phase behavior, our calculations also give detailed information on the microscopic state of the self assembled system. These include average aggregated size, orientational order parameter, and inter columnar spacing in the columnar phase. As expected, the average aggregate size increases monotonically with increasing concentrations as well as with decreasing temperature [16–18].

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

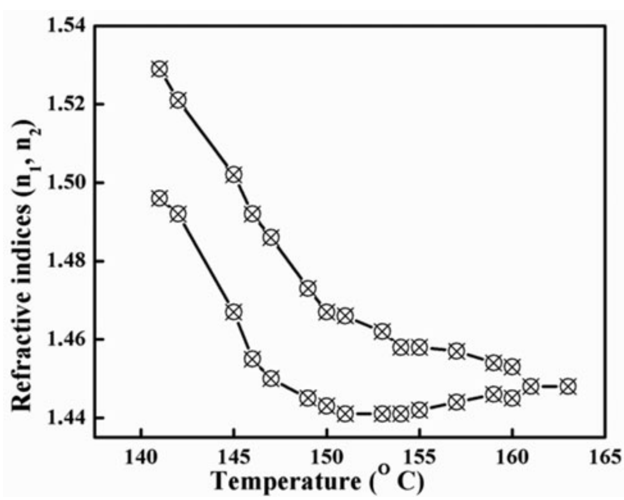


Figure 4. Temperature variations of refractive indices for the mixture of 52% abietic acid and ethylene glycol.

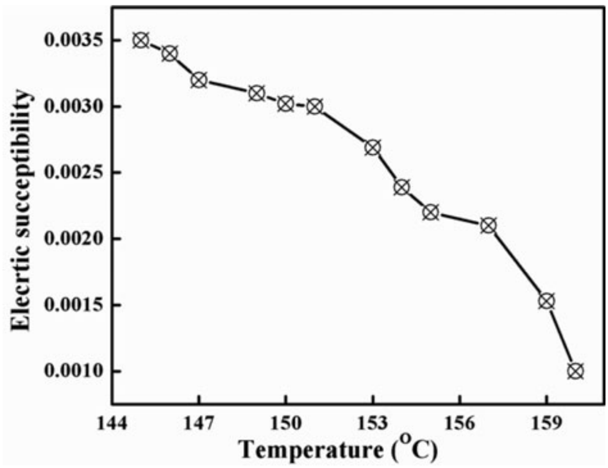


Figure 5. Temperature variations of electrical susceptibility for the mixture of 52% abietic acid and ethylene glycol.

different temperatures for different concentrations using Abbe Refractometer and Precession Goniometer Spectrometer. The temperature variations of refractive indices for 52% of abietic acid in ethylene glycol are as shown in Fig. 4. The value of n_e is greater than n_o, indicating that the material is uniaxial positive. The values of electrical susceptibility for 52% of abietic acid in ethylene glycol have been calculated using Neugebauer relation [19] at different temperatures. The temperature variations of electrical susceptibility for the mixture are as shown in Fig. 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 columnar

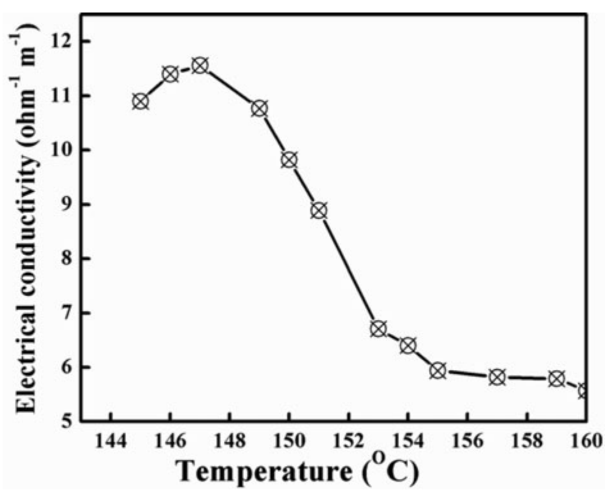


Figure 6. Temperature variation of electrical conductivity σ (Ω^{-1} m^{-1}) for the mixture of 52% of abietic acid in ethylene glycol.

biphasic region of chromonic liquid crystalline phases. Further, with increase in the concentration of abietic acid, the value of electrical susceptibility decreases with temperature. This is because, the effective optical anisotropy associated with the molecules of abietic acid decreases.

Conductivity Measurements

To obtain reliable data on the phase behavior with temperature, electrical conductivity measurements are necessary. An abrupt change of electrical conductivity with temperature relates to the phase behavior of lyotropic and thermotropic systems [20, 21]. The temperature variations of electrical conductivity in the present case are as shown in Fig. 6. As it can be seen from Fig. 6, there is some change in the value of electrical conductivity up to 155°C during cooling from the isotropic phase in case of the mixture with 52% concentration of abietic acid. With further decrease in temperature, the electrical conductivity goes on increasing up to 147°C and below this; the electrical conductivity starts to decrease as we move toward the room temperature. Thus, for the mixture with 52% concentration of abietic acid, though there is a change of phase from C+I to C, there is no immediate appreciable change in the value of electrical conductivity. The change is observed only after further cooling and this suggests that the size of aggregates starts growing below 155°C and the system moves toward more orderliness. Finally, below 147°C the size of aggregates becomes so large that the specimen starts moving toward crystalline nature.

Conclusions

Microscopic investigation of the binary mixture of abietic acid and ethylene glycol shows a molecular orientation of co-existent biphasic region of aggregated columnar (C+I) and columnar (C) phases for different concentrations of abietic acid at higher temperatures. Observations from different studies, unconventional sequence indicates that, the mixture clearly exhibits a lyotropic chromonic liquid crystalline nature. Birefringence study shows the contribution of birefringence of given binary mixture is mainly due to abietic acid. A change in the value of electrical conductivity with temperature implies that, when the given mixture is cooled from isotropic phase, the aggregated molecular size 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.

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