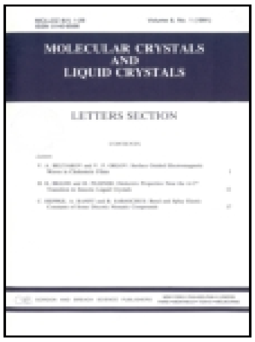

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Co-existent Biphasic Region of Nematic Phase in Binary Mixture of Abietic Acid and Glacial Acetic Acid

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We report the results of our studies on the optical and thermal properties of binary mixture of compounds viz., Abietic acid and Glacial acetic acid. The mixture exhibits very interesting chromonic nature of co-existent biphasic region of nematic phase for different concentrations of Abietic acid sequentially when the specimen is cooled from its isotropic phase. The order parameter (S) of nematic phase is estimated with the help of optical anisotropy using the measured refractive index and density data. The temperature variation of experimentally found order parameter curve is well fitted with the Maier–Saupe theoretical curve. The temperature variation of electrical-conductivity has also been discussed. Formation of above molecular orientations has been confirmed by optical and DSC studies.

Keywords Binary mixture; chromonic; molecular orientation; nematic; order parameter

Introduction

Chromonic systems are the lyotropic/thermotropic liquid crystalline phases, which are formed by soluble aromatic compounds, which occur as result of face-to-face aggregation of the molecules into columns. There are two principal chromonic phases; the N phase which consists of a nematic array of columns at higher concentrations and the M phase, in which the columns lie in an hexagonal array. Chromonic phases are formed by a range of multi-ring aromatic compounds including drugs, dyes, and nucleic acids. They have characteristic multi-peritectic phase diagrams and distinctive optical textures. The exploitation of the unique properties of chromonic systems has scarcely started.

Now recent studies shows the combination of self-ordering, ease of alignment, sensitivity to change the conditions of additives, coupled with their optical properties and electro-optical properties, makes possible a range of sophisticated devices, including polarizers, optical compensators, light-harvesting devices and micropatterned materials and the fact that they are water-based, suggests a future role in biosensors for medical diagnosis [1–5].

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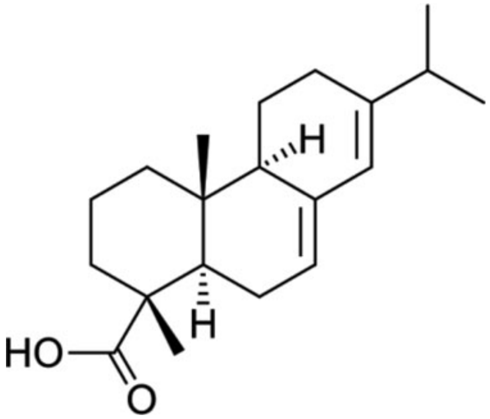

Figure 1. **(a)**. Structural formula of the Abietic acid molecule.

In the present investigation, we have shown the existence of chromonic nature of molecular orientation of co-existent biphasic region of nematic (N + I) and lyotropic nematic (N) phases in binary mixture of abietic acid and glacial acetic acid (GAA). 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 understand the coupling between structure of the orientated molecules and the order of mesophases in this observation regarding lyotropic chromonic liquid crystals, wherein it has been observed that, the segregated molecules formed at low concentrations are not large enough to align, and at larger concentrations, the segregated molecular size increases into supra-molecular assemblies.

Experimental

The compound Abietic acid used in this investigation was obtained from the Basic Pharma Life Science Pvt., Ltd., India, and it was further purified twice by a re-crystallization method using benzene as a solvent. GAA was supplied from Kodak, Ltd., Kodak house, Mumbai, India. The structural formulae for abietic acid and glacial acetic acid molecules are as shown in Fig. 1(a, b). Mixtures of 25 different concentrations of abietic acid in GAA were prepared and they were mixed thoroughly. These mixtures were kept in desiccators for six hours. Samples were subjected to several cycles of heating, stirring, and centrifuging to

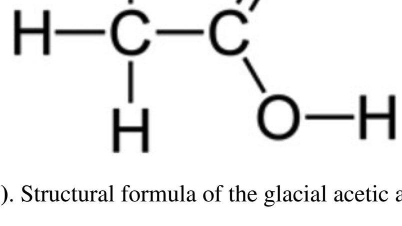

Figure 1. **(b)**. Structural formula of the glacial acetic acid molecule.

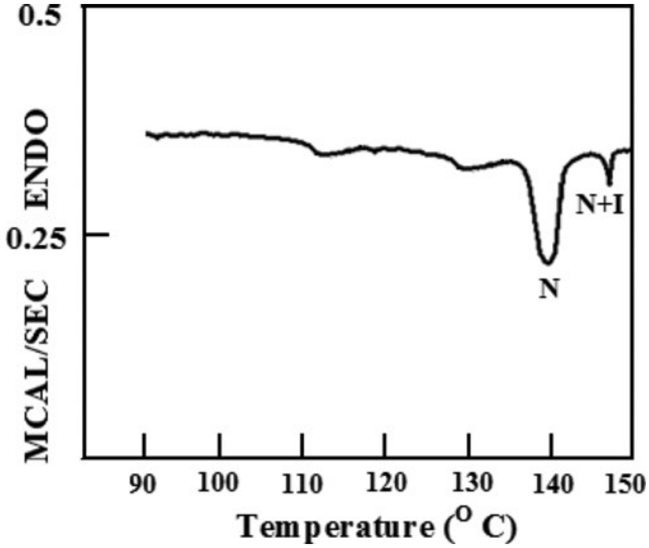

Figure 2. DSC thermogram for the sample of 30% of Abietic acid and glacial acetic acid

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 mixture of all concentrations using the Perkin-Elmer DSC II Instrument facility available at Raman Research Institute, Bangalore, India. The DSC thermogram for the sample of 30% of abietic acid in glacial acetic acid is shown in Figure 2. The sequence of occurrence of chromonic nature of liquid crystalline phases observed is as follows;

I—148°C, $N + I$—140°C, N—below 140°C.

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. 3, which is drawn by considering the phase transition temperatures against the concentrations of the given mixture, clearly illustrates that, the mixtures with concentrations from 10% to 60% of abietic acid in glacial acetic acid exhibit very interesting co-existent biphasic region of nematic ($N + I$) and lyotropic nematic (N) phases, which are the characteristic of chromonic liquid crystalline phases, respectively, at different temperatures and different concentrations. Our experimental studies on phase transitions are similar to the observations of Raja et al., [6,7]. In the present study, Fig. 2 clearly illustrates that, the $N + I$ phase transition is of first order. Here we propose the phase transition from $N + I$ to I is to be of first order, looking into small enthalpy change [8] at this transition. Segregation of the molecules increases as the temperature decreases.

It is well known that, the molecular orientation of phase transition between I and $N + I$ phase is of first order, whereas, the molecular orientation of phase transition between $N + I$

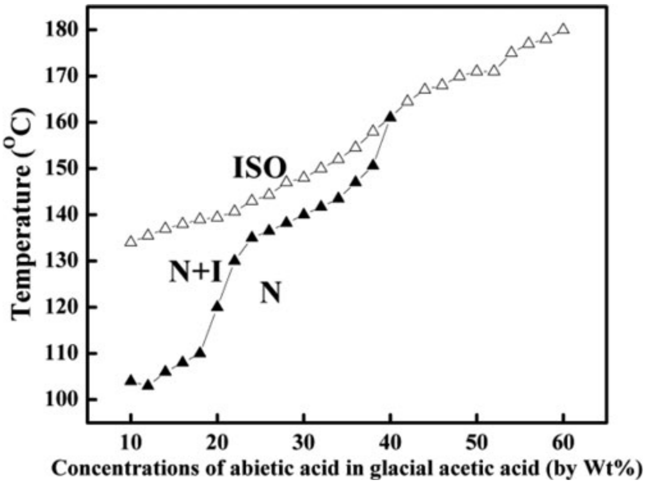

Figure 3. Partial phase diagram for the mixture of Abietic acid and glacial acetic acid.

and lyotropic nematic (N) phase may be of either first order or second order depending upon the coupling between the orientational order and positional order, which in turn depends on the width of the lyotropic nematic (N) phase. It also known that, a chromonic liquid crystal with a wide lyotropic nematic (N) phase is more likely to exhibit a first order $N + I$ to lyotropic nematic (N) phase transition [9]. Since the width of the lyotropic nematic (N) phase in the present case is wide, the $N + I$ to lyotropic nematic (N) phase transition has been treated to be of first order. The chromonic nature of co-existence biphasic region of nematic $N + I$ and lyotropic nematic (N) phase was identified on the basis of microscopic texture and the fact that they spontaneously orient in a strong magnetic field. The chromonic system of co-existent biphasic region of nematic $N + I$ phase of plank-shaped molecular aggregates $(N + I)_{\mathrm{P}}$ and rod-like aggregates $(N + I)_{\mathrm{R}}$ occur at different temperatures, once the concentration of given molecules exceeds from lower to higher in some lyotropic chromonic systems.

The observations indicate that, given mixture exhibits a lyotropic chromonic liquid crystalline nature [10]. For lower concentrations and/or higher temperatures, some aggregates are showing the preferred direction for alignment and others remain randomly oriented. At this stage, in this region, up to 10% concentration of abietic acid, the molecular orientations are not clear to show any of the liquid crystalline phases. The aggregates are getting aligned and showing the $N + I$ and lyotropic nematic (N) phases in concentrations from 10% to 60% are at different temperatures. Some concentrations ranging from 10% to 40% of abietic acid show a co-existent biphasic region of nematic ($N + I$) phase at different temperatures. With the increase in concentration of abietic acid, the co-existent biphasic region of nematic ($N + I$) phase decreases and the lyotropic nematic (N) phase increases.

Optical Texture Studies

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. Up to 10% concentrations of abietic acid, the aggregates are not clear. The co-existent biphasic region of nematic ($N + I$) and lyotropic nematic (N) phases are clear from 10% of abietic acid onwards. In present work, the concentration ranging from 10% to 60% of abietic acid has been considered for the discussion. In mixture with concentrations ranging from 10% to 40% of abietic acid, the aggregates are aligning along a particular direction and hence exhibiting a co-existant biphasic region of nematic ($N + I$) phase at higher temperatures. When the specimen with 30% abietic acid 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, which are identified as chromonic nature of co-existent biphasic region of nematic ($N + I$) phase and is as shown in Fig. 4 (a). On further cooling, $N + I$ phase changes over to lyotropic nematic (N) phase as shown in Fig. 4 (b); it remains up to room temperature. Here it is pertinent to remark that the molecular segregation increases towards the room temperature. In lyotropic nematic N phase, the molecules are stacked to form long columnar aggregates which align parallel to each other. There is no long-range positional order among the columns. Here it is very interesting to note that the co-existent biphasic region of nematic $N + I$ phase decreases with increasing the concentrations of abietic acid, whereas lyotropic nematic (N) phase increases, respectively, at different temperatures.

Chromonic liquid crystals hold great promise to applications as optical materials and devices in technology. Potential applications reported for chromonic liquid crystals include biosensors [11–13], polarizing films [14–18], optical retardation plates [19, 20] and micro-patterned polarizing elements for stereoscopic displays [21, 22].

Birefringence Studies

The molecular orientations of co-existent biphasic region of nematic phase in lyotropic system are generally formed by amphiphilic aggregation with bilayer structure [23]. As in case of co-existent biphasic region of nematic phase of thermotropic/lyotropic system, the bilayer amphiphilic aggregations show some degree of parallel orientation, which is responsible for the macroscopic anisotropy of liquid crystalline phases. Birefringence study helps us to understand the optical anisotropic properties of the samples. The orientational order parameter of the nematic phase is essential to understand the degree of orientations of the molecules.

In the present investigation, we have measured the temperature variation of refractive indices (n_1 and n_2) and densities for the mixture with different concentrations by using Abbe Refractometer and Precision Goniometer spectrometer at the wavelength 5893 Å in the region of nematic phase. The sample whose refractive indices have to be determined is introduced between two prisms of the Abbe refractometer [24]. The combination of prisms containing liquid crystalline material is illuminated by a monochromatic light. The refractometer is in conjunction with a temperature bath from which hot water can be circulated to maintain the sample at different temperatures. In the field of view, two lines of demarcation of slightly different polarization are observed. The horizontal polarization corresponds to the ordinary ray and vertical polarization is due to the extraordinary ray. By matching the cross-wire, the refractive indices of the ordinary ray and extraordinary ray are read directly. Refractive index n_1 due to extraordinary ray and n_2 due to ordinary ray respectively have been determined. Saupe has used the modified Lorentz–Lorentz [25] formula for the calculation of orientational order parameters of the given thermotropic and lyotropic systems.

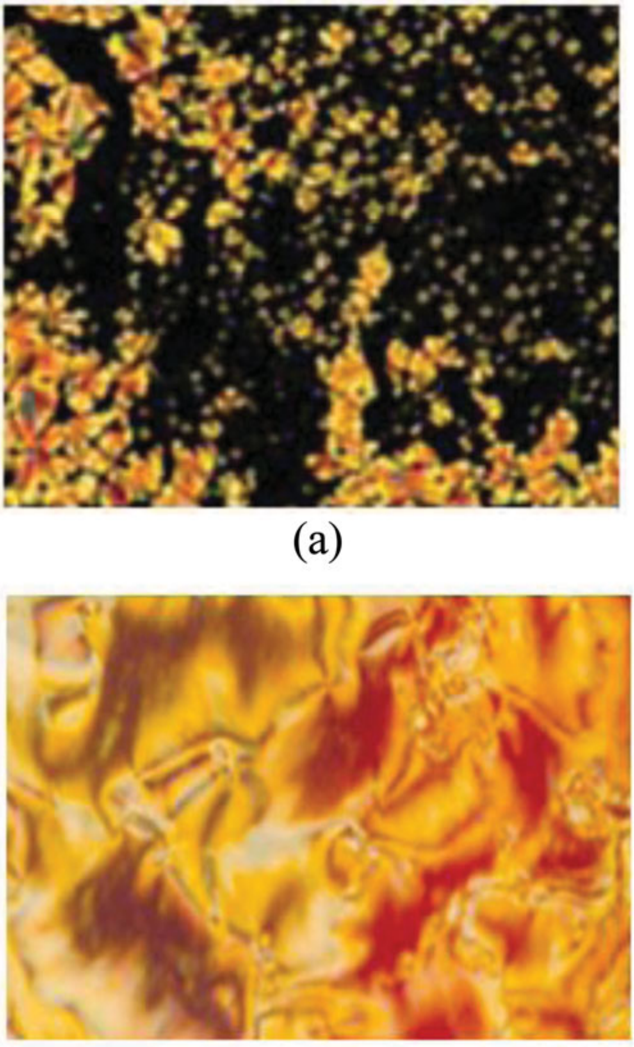

Figure 4. Microphotographs obtained in between the crossed polars, (a) Co-existent biphasic region of aggregated nematic ($N + I$) phase (250×). (b) Lyotropic nematic (N) phase (250×).

For the estimation of orientational order parameter of nematic phase, we assume only the birefringence of the abietic acid molecules [23]. The optical anisotropy ($\Delta\alpha$) contribution from acetic acid is neglected because the concentration of abietic acid molecules is increased in the mixture. $S = \frac{1}{2}[3\cos^2\theta - 1]$ is the degree of order of the abietic acid molecules, where θ is the angle between the long molecular axis and optic axis of the molecular aggregation in the region of nematic phase, $\cos^2\theta$ is the average over the molecular orientation.

In order to estimate the value of optical anisotropy ($\Delta\alpha$) of abietic acid molecule, the value of polarizability along the axis of the molecules and the polarizability perpendicular to the long axis of the molecule. The value of effective polarizability of each molecule

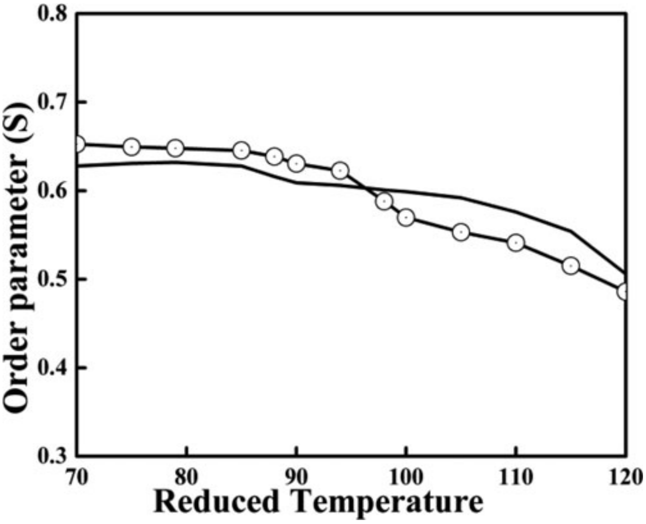

Figure 5. Temperature variation of order parameter of the nematic phase.

is calculated from the optical anisotropy of bond polarizability data for the wavelength 5893 Å [26] assuming that the molecules have all trans-configuration, the value of $\Delta\alpha$ is estimated [27]. The order parameter (S) of the nematic phase has been calculated with the help of ($\Delta\alpha$) value. The order parameter (S) value of the mixture was estimated at different temperatures for different concentrations. Boden et al. [28] have pointed out in their study that the variation of birefringence with temperature is dependent upon both the size and shape of the molecular aggregation, in addition to their dependence on orientational order. However, we also notice that the order parameter varies with mole percent of abietic acid and it is observed that order parameter (S) decreases with decreasing the concentrations of abietic acid. The temperature variations of order parameter (S) of the nematic phase is as shown in Figure 5, and the experimental values of order parameters are compared with the Maier–Saupe theoretical curve. It is observed that the variation of order parameter (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 [29,30].

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 corresponds to the phase behavior of lyotropic and thermotropic systems [31]. The temperature variation of electrical-conductivity is shown in Fig. 6. From the graph, it is clear that the conductivity of the material with respect to temperature is nearly constant toward higher temperatures. This indicates that there is no much variation in the structure and aggregation of molecules of the liquid crystal. However, conductivity varies significantly upon cooling, which may be due to the transformation of its phase [32]. From the graph, it is evident that there is a drastic change in electrical-conductivity at temperatures 139°C and 148°C, which correspond to molecular orientation from $N+I$ to N phases and I to $N+I$ phase, respectively. The origin of these effects seems to lie not only in electrostatic interactions, but also depends on the participation of solvent in

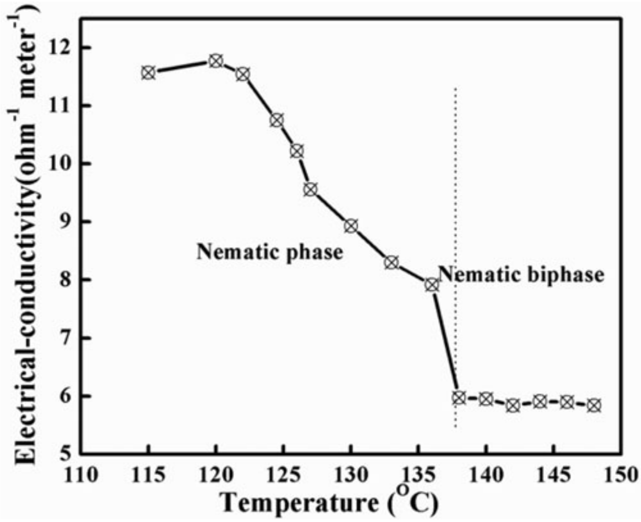

Figure 6. Temperature variation of electrical-conductivity σ (Ω^{-1} m^{-1}) for the sample of Abietic acid and glacial acetic acid.

aggregation of molecules. This type of behavior is observed in columnar and hexagonal phase of molecular orientations of lyotropic and thermotropic liquid crystals [33]. These sudden changes cannot be thought of only due to change in the orientation of molecules. Also, they can be attributed to changes in the dimension of discs along with change in their molecular orientation.

Conclusions

Microscopic investigation of binary mixture of abietic acid and glacial acetic acid shows the existence of chromonic system of molecular aggregation of co-existent biphasic region of nematic $(N + I)$ phase for different concentrations, respectively, at different temperatures. The observation from the various studies of this unconventional sequence clearly indicates that the mixture exhibits a lyotropic chromonic liquid crystalline nature. At lower concentrations of abietic acid, the molecular orientations are not aligned and they start aligning as the concentration increases at higher temperatures. Drastic changes in the values of electrical-conductivity with the variation of temperature unambiguously correspond to molecular orientations of lyotropic chromonic phase at different temperatures. Changes in electrical-conductivity are expected to be due to changes in the dimension of discs along with changes in the orientational order of the molecule. DSC studies also lend support to these observations. It is observed that the variation of order parameter values is in good agreement with the Maier–Saupe theoretical curve.

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