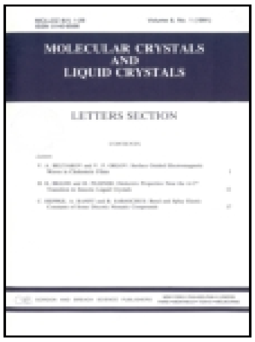

Molecular Crystals and Liquid Crystals

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Optical and Thermal Studies on Lyotropic Chromonic Liquid Crystals in Nematic and Biphasic Regions

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A binary mixture of abietic acid and orthophosphoric acid (H_3PO_4) exhibits coexistence of biphasic region of Nematic + Isotropic (N + I), lyotropic Nematic (N_D), and Smectic-G (SmG) phases. The mixture exhibits N + I, N and SmG phases at different concentrations and at different temperatures. Mixtures with all concentrations of abietic acid exhibit I→N + I→N→SmG phases sequentially when the specimen is cooled from its isotropic melt. These phases have been characterized by using differential scanning calorimetric, X-ray diffraction, and optical texture studies.

Keywords Binary mixture; biphasic region; lyotropic nematic phase; molecular orientation; optical anisotropy; phase formation

Introduction

Liquid crystals are considered as the fourth state of matter [1], their properties are intermediate between that of the crystalline solid state and that of the liquid state. Liquid crystals flow like a liquid, but they are anisotropic compounds [2, 3]. The refractive index, electric permittivity, magnetic susceptibility, and the mechanical properties of a liquid crystal depend on the direction in which these quantities are measured. Typical liquid crystals have either a rod-like or disk-like shape, although many exceptions on this basic motif have been described [4–7].

Most of the liquid crystals are neutral organic compounds. In metallomesogens, a metal is incorporated in the molecule of the liquid-crystalline compound [8–18]. Also minerals or inorganic compounds can form liquid crystalline phases [19–22]. Driving forces for the formation of a liquid-crystalline phase are interactions between the anisometric molecules (dipole–dipole interactions, van der Waals interactions, π–π stacking ...). Ionic liquid crystals are a class of liquid-crystalline compounds that contain anions and cations. The ionic character means that some of the properties of the ionic liquid crystals differ significantly from that of conventional liquid crystals. Typical for ionic liquid crystals is the ion conductivity. The ionic interactions tend to stabilize lamellar mesophases, but

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ionic liquid crystals also display uncommon mesophases such as the nematic columnar phase.

Ionic liquid crystals can be considered as materials that combine the properties of liquid crystals and ionic liquids. Worldwide intense research activity in the field of ionic liquids is presently going on [23–29]. The main driving force to explore ionic liquids is the fact that these compounds have a very low vapor pressure, so that they are candidates to replace volatile organic solvents in organic reactions. Because the properties of ionic liquids (miscibility with water and other solvents, dissolving ability, polarity, viscosity, density ...) can be tuned by an appropriate choice of the anion and the cation, ionic liquids are often considered as designer solvents. These ionic liquids can also be used to immobilize transition metal catalysts in the liquid phase of biphasic catalytic reactions. Other applications include their use as solvents for extraction processes and as an electrolyte for batteries, fuel cells, and dye-sensitized solar cells.

In the present investigation, we have shown the coexistence of biphasic region of Nematic + Isotropic (N + I), Nematic (N_D), and smectic-G (SmG) phases, respectively, at different concentrations in the binary mixture of abietic acid and orthophosphoric acid (H_3PO_4). 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 [30, 31], 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 Section

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 recrystallization method using benzene as a solvent. Orthophosphoric acid (H_3PO_4) was supplied from Kodak, Ltd., Kodak house, Mumbai, India. Mixtures of different concentrations of abietic acid and orthophosphoric acid (H_3PO_4) were prepared and were mixed thoroughly. The concentrations of these mixtures were kept in desiccators for a long time. The samples were subjected to several cycles of heating, stirring, and centrifuging to ensure homogeneity. The phase transition temperatures of these concentrations were measured with the help of Leitz-polarizing microscope in conjunction with a hot stage. The samples were sandwiched between the slide and cover slip and were sealed for microscopic observations. The differential scanning calorimetry (DSC) thermograms were taken for the mixtures of all concentrations using Perkin-Elmer DSC II Instrument facility available at Raman Research Institute, Bangalore, India. The X-ray broadening peaks were obtained at different temperatures using JEOL diffractometer. The density and refractive indices in the optical region are determined at different temperatures by employing the techniques described by the earlier investigators [32, 33].

Phase Diagram

Mixture of abietic acid in orthophosphoric acid (H_3PO_4) exhibits very interesting different liquid crystalline phases and the phase transition temperatures are measured by using Leitz-polarizing microscopic. The partial phase diagram is shown in Figure 1, and it is

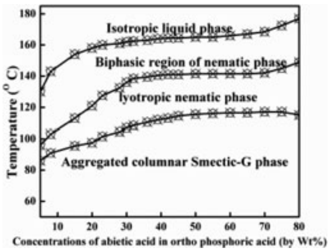

Figure 1. Partial phase diagram for the mixture of abietic acid in orthophosphoric acid (H_3PO_4).

obtained by plotting the concentrations against the phase transition temperatures of the given mixture, which clearly illustrates that the mixture of all concentrations of abietic acid in orthophosphoric acid (H_3PO_4) exhibits biphasic region of nematic, lyotropic nematic, and aggregated SmG phases, respectively, at different temperatures, when the specimen is cooled from its isotropic liquid phase. The concentrations of the mixture from 5% to 80% of abietic acid show an very interesting unusual behavior of chromonic nature of coexistent biphasic region of nematic (N + I), lyotropic nematic (N_D) and smectic-G (SmG) phases. The smectic-G phase remains up to room temperature.

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 the slide and cover glass. All concentrations of abietic acid, chromonic molecules have a strong tendency to stack into aggregates. A larger number of aggregates produce a poly-disperse system of linear aggregates [34, 35] that can arrange themselves into ordered chromonic liquid crystalline phases as a function of concentrations and temperature.

Mixture of 36% of abietic acid 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 coexistent biphasic region of nematic N + I phase and the texture as shown in Fig. 2(a). On further cooling, N + I phase changes over to lyotropic nematic (N_D) phase. The lyotropic nematic (N_D) phase produces a schlieren texture with disclinations and point defects-boojums (with four brushes of extinction) [36]. The lyotropic nematic (N_D) phase as shown in Fig. 2(b). On further cooling, the lyotropic nematic (N_D)

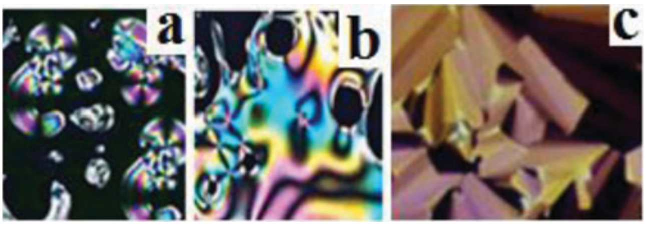

Figure 2. Microphotographs obtained in between the crossed polars, (a) coexistent biphasic region of nematic (N + I) phase (250×). (b) Lyotropic nematic (N_D) phase (250×). (c) Smectic-G phase (250×).

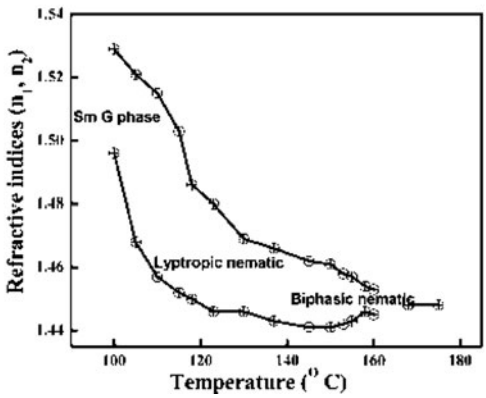

Figure 3. Temperature variations of refractive indices for the mixture of 36% abietic acid in ortho phosphoric acid (H_3PO_4).

phase slowly changes over to aggregation of smectic-G phases, respectively, at different temperatures. The aggregated smectic-G is as shown in Fig. 2(c). Due to exhibition of this behavior, chromonic liquid crystals hold great promise to applications as optical materials and devices [37–48]. This type of phase changes cannot be thought not only due to change in orientation of the given mixture, but they can be attributed to changes in the dimension of disks along with changes in orientation [49].

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 36% of abietic acid in orthophosphoric acid (H_3PO_4) are as shown in Fig. 3. The value of n_e is greater than n_o, indicating that the material is uniaxial positive. The values of electrical susceptibility for 36% of abietic acid in orthophosphoric acid (H_3PO_4) have been calculated using Neugebauer relation [50] at different temperatures. The temperature variations of electrical susceptibility for the mixture are as shown in Fig. 4. 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 liquid crystalline phases. Further, with increase in the concentration of abietic acid, the value of electrical susceptibility decreases with temperature, because the effective optical anisotropy associated with the molecules of abietic also decreases.

X-Ray Studies

The X-ray diffractometer traces obtained for the mixture of 36% of abietic acid at temperatures 100, 125, and 150°C are shown in the Fig. 5, the diffraction peaks at these temperatures correspond to smectic-G, lyotropic nematic (N) and biphasic region of nematic (N + I) phases, respectively, using JEOL diffractometer with the settings: TC4, CPS400, channel width 100 for $\lambda = 1.934$ Å. XRD method appears to be only the practical and reliable way to find the crystalline size measurement [51–53] of the different liquid crystalline materials.

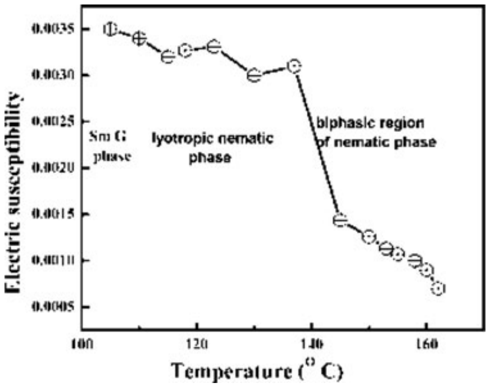

Figure 4. Temperature variation of electric susceptibility for the mixture of 36% abietic acid in orthophosphoric acid (H_3PO_4).

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 a broadening of the diffraction peaks. In order to estimate the crystalline size of materials from the broadening of corresponding 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 move from crystalline phase to amorphous region [54, 55], which clearly illustrates that, the crystalline size of the liquid crystalline materials decrease with increasing the temperature. Here in the Fig. 5, coexistence of biphasic region of nematic (N + I) phase is energetically not stable, because the molecular ordering of the

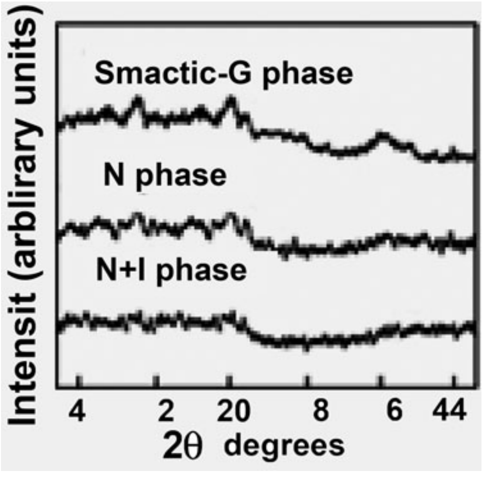

Figure 5. XRD traces obtained for the mixture 36% of abietic acid in orthophosphoric acid (H_3PO_4) at different temperature.

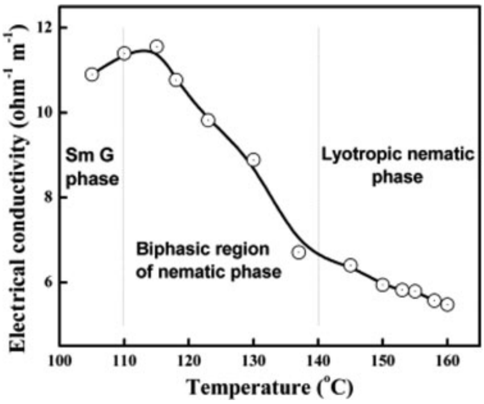

Figure 6. Temperature variation of electrical-conductivity σ ($\times 10^{-9}\ \Omega^{-1}\text{m}^{-1}$) for the sample 36% of abietic acid in orthophosphoric acid (H_3PO_4).

particular phase is not clear. Hence it is very difficult identify the intensity of peak in N + I phase. The lyotropic nematic (N) phase is also energetically not stable and it shows the molecular ordering of the nematic phase, hence it shows the intensity of four small peaks. The crystalline size of the nematic phase is 35.6125 nm and the smectic-G phases are more stable for large crystallite is 47.9864 nm. From the X-ray studies, we have been observed that the molecular ordering of the liquid crystalline phase increases with decreasing the temperature. The coexistent biphasic region of (N + I) phase transform into lyotropic nematic (N_D) phase and lyotropic nematic (N_D) phase transform into smectic-G phases, sequentially when the specimen is cooled from its isotropic phase, it clearly illustrates that, the crystalline size of the liquid crystalline materials are big enough to indicate that, the molecular ordering [56] of layer structure increases as well as decrease the temperature.

Conductivity Measurements

We have to obtain a 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 [50]. The temperature variations of electrical-conductivity as shown in Fig. 6, which clearly illustrates that, there are some changes in the value of electrical conductivity from 110to 140°C and 140 to 160°C, while the mixture of 36% abietic acid cooling from isotropic phase. For the mixture of 36% abietic acid, the sequence of phase changes from smectic-G phase to lyotropic nematic (N_D) phase and lyotropic nematic (N_D) phase to coexistent biphasic region of nematic (N + I) phase. In the figure if we notice that, if there is some appreciable changes observed in the value of electrical conductivity, the electrical conductivity increases as the temperature moves towards the crystalline phase. Since it suggests that, the sizes of aggregate molecule start to grow towards the crystalline phase of aggregated smectic-G phase. Finally, below 110°C, the aggregated molecular size becomes so large, that the specimen starts moving towards crystalline nature [57–59].

Conclusions

Microscopic investigation of the binary mixture of abietic acid and orthophosphoric acid (H_3PO_4) shows the molecular orientation of coexistent biphasic region of nematic ($N + I$) and lyotropic nematic (N_D) phase and smectic-G phases for different concentrations of abietic 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. 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. But below a particular temperature, the size of aggregates becomes so large, that the specimen moves towards crystalline nature. X-ray studies lend support to the grain size of the different liquid crystalline phases.

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