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Phase Transition and Optical Characterization of Mesophase Stability of Nematic and Columnar Biphasic Regions

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ABSTRACT

We report the results of our studies on the optical and thermal properties of binary mixture of two compounds viz., abietic acid and alizarin dye. The mixture shows a very interesting co-existent biphasic regions of nematic (N + I) and columnar smectic (C + I) phases, sequentially when the specimen is cooled from its isotropic phase respectively at different concentrations of given molecule. The temperature variations of optical anisotropy, optical textures and electrical conductivity have also been discussed. Aggregated molecular size has been confirmed by X-ray studies.

KEYWORDS

Binary mixture; columnar phase; chromonic system; molecular aggregation; optical anisotropy

Introduction

During the last four decades, a lot of research and development has been done in the field of liquid crystals for their use in display applications. The important features required for this application are flatness, low power consumption, compactness leading to low weight, and full color capability [1]. The liquid crystalline display [2] that uses a liquid crystal and dye mixture has received much more attention because of its wide viewing angle, daylight readability, high brightness and no requirement of polarizer's. Dye-doped liquid crystals have received substantial interest in the recent decade in the development of optical applications owing to their high birefringence and highly flexible optical controllability via manipulation of the interaction of liquid crystals with the photo excited dyes [3–5]. The microscopic mechanisms are not still clearly understood and quite often experimental results still reveal unexpected behaviors [6–9]. The addition of dyes into nematic liquid crystals, even in small concentrations, introduces new orienting mechanisms [6]. Mixing of carbon nanotubes in liquid crystal host is the recent development toward the modification of physical properties of liquid crystals by doping nonmesogenic molecules [10, 11].

In the present work, we have considered the mixture of alizarin dye and abietic acid. The co-existent biphasic regions of nematic (N+I) and columnar smectic (C + I) phases have been observed using optical microscopic technique, and they have been also verified from the results of X-ray and optical anisotropic techniques [12, 13].

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Experimental studies

Mixtures of 25 different concentrations of alizarin dye in abietic acid were prepared, and they were mixed thoroughly. The mixtures were kept in desiccators for 6 hrs. 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. The samples were sandwiched between the slide and cover slip and were sealed for microscopic observations. 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.

Result and discussions

Optical studies

The molecular orientation of optical textures exhibited by the samples was observed and recorded using 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. All concentrations of dye, abietic acid molecules have a strong tendency to stack into aggregates. A larger number of molecular aggregates produce a polydisperse system [14, 15], that can arrange themselves into ordered co-existent biphasic regions of chromonic liquid crystalline phases as a function of concentrations and temperature of the given mixture. Biphasic regions of chromonic liquid crystals such as N + I, C + I, and N + C phases is 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 [16, 17]. The 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, chromonic molecules do not form micelles, nor do they show any appreciable surface activity. However, in the presence of alizarin dye, the abietic acid molecules tend to aggregate into stacks due to both weak Vander Waals interactions between the cores and the hydrophobic effect. All concentrations of dye, if there observed a degree of molecular orientation, as the concentration of dye increases, the molecular aggregated size increases. If the dye concentrations are high enough, the mechanism of molecular aggregated size in lyotropic chromonic liquid crystal is analogous to the worm-like micelles formed by surfactant molecules in solutions. The aggregated size grows definitely, if the entropy increases when the number of aggregates decreases. The stability of these phases depends on both temperature and concentration. Figure 1 shows the phase diagram and typical texture of alizarin dye and abietic acid mixture. The phase diagram shows an very interesting calamitic thermotropic nematic (N) phase and the aggregation of columnar (C) phase and also with co-existent biphasic regions of nematic (N + I) and aggregated columnar smectic (C + I) phases, respectively, at different temperature and at different concentrations of dye molecules.

Mixture of 10% to 30% of alizarin dye is cooled from its isotropic liquid phase, a genesis of nucleation starts in the form of molecular orientations, which grow and segregate the molecules, which identified as co-existent biphasic region of nematic (N + I) phase and the texture as shown in Fig. 2(a). On further cooling the specimen, N + I phase changes over to calamitic thermotropic nematic (N) phase and this phase produces a schlieren texture with

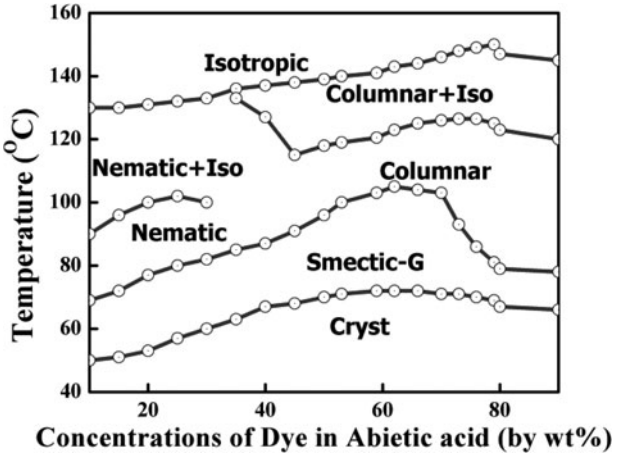
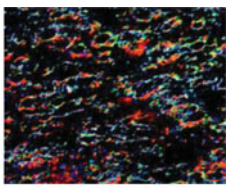


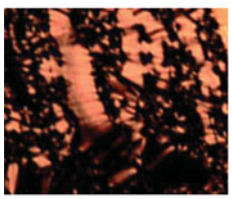
Figure 1. Partial phase diagram for the mixture of alizarin dye and abietic acid.

disclinations (characterized by two dark brushes of extinction) and point defects-boojums (with four brushes of extinction) [18].

Above 35% of alizarin dye, the binary mixture exhibits a co-existent biphasic region of columnar smectic (C + I) phase as shown in Fig. 2(b). In this phase, molecules are stack to form long columnar aggregates which align parallel to each other. There is long-range positional order among the oriented molecules. On further cooling at different temperatures, co-existent biphasic region of columnar smectic (C + I) phase slowly changes over to columnar (C) phase, respectively. Due to exhibition of this behavior, chromonic liquid crystals hold great promise to applications as optical materials and devices [19–30]. Here it is pertinent to remark that, at low concentrations of dye with abietic acid molecule exhibits N + I phase and high concentrations of dye with abietic acid molecules show C + I phases. This type of behavior observed only in chromonic liquid crystal system [31]. For samples having the concentration of alizarin dye above 30% and below 35%, the optical textures are not clear. In this region, the sample shows viscous nature. But in the concentrations range from 10% to 90% of the given mixtures, the molecular orientations of calamitic thermotropic nematic (N)



a)



b)

Figure 2. Microphotographs showing, (a) Co-existent biphasic region of columnar nematic (N + I) phase (180×). (b) Co-existent biphasic region of columnar smectic (C + I) phase (180×).

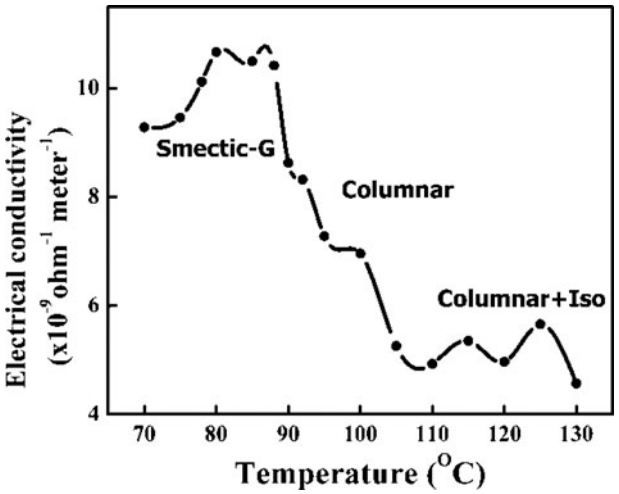


Figure 3. Temperature variation of electrical-conductivity σ (x 10^{-9} Ω^{-1} m^{-1}) for the sample of 45% of alizarin dye and abietic acid.

and columnar smectic (C) phases are not a stable and then changes over to SmG phase. The molecules in the SmG phase are packed within the layers, having their long axes tilted with respect to normal to the layer planes [32].

Conductivity measurements

Electrical-conductivity measurements help in getting better idea on the phase behavior with temperature. A change in the electrical conductivity with temperature relates to the phase behavior of lyotropic, thermotropic, and chromonic liquid crystalline systems [33]. The temperature variations of electrical conductivity are shown in Fig. 3, which clearly illustrates that there is some change in the value of electrical conductivity from 70°C to 130°C, while cooling from isotropic phase for the mixture of 45% alizarin dye. For the mixture of 45% alizarin dye, the sequence of phase changes from co-existent biphasic region of columnar smectic (C + I) phase to smectic-G phases. Here it has been found that the electrical conductivity goes on increasing as the temperature decreases. This suggests that aggregated molecular grain size start to grow towards decreasing the temperature and then the system becomes more orderly [34, 35].

Characterization of nano aggregation

The X-ray diffractometer traces obtained for the mixture of 45% of alizarin dye at temperature 100°C and 85°C are as shown in Fig. 4, the diffraction peaks at these temperatures correspond to columnar (C) phase and smectic-G phase respectively by using JEOL diffractometer with the settings: TC4, CPS400, channel width 100 for $\lambda = 1.934$ Å. X-ray diffraction study is an important method to determine the nano-aggregated grain size of the molecules for different liquid crystalline phases [36, 37]. The deviation from perfect liquid crystallinity leads to broadening of the diffraction peaks. In order to estimate nano-aggregated grain size of the molecules for different liquid crystalline phases corresponding to broadening of X-ray diffraction peaks we have used the Scherrer's formula

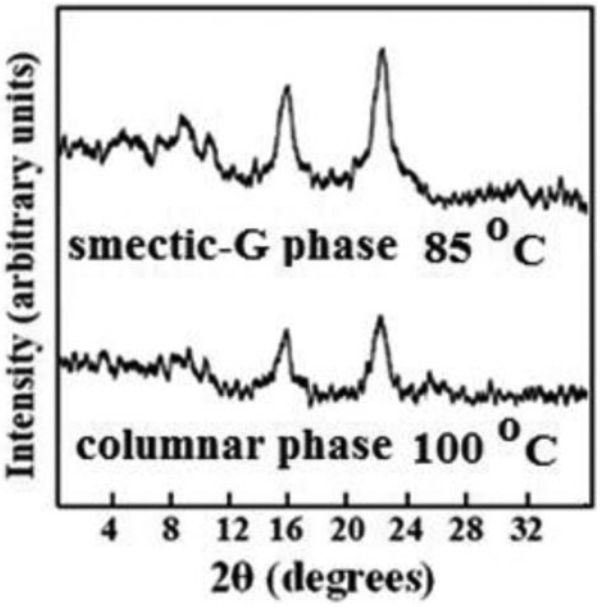


Figure 4. X-ray broadening spectrum for the mixture of 45% of alizarin dye and abietic acid at different temperatures of columnar (C) and smectic-G phases.

$$L = K\lambda/\beta\cos\theta \tag{1}$$

where L is the nano-aggregated grain size, λ is the wave length of X-ray radiation (Fe: 1.934 Å), K is usually taken as 0.89, β is the line width at half maximum and θ is the diffraction angle. Usually with decrease of temperature [38, 39], the nano-aggregated grain size of the molecules increases. From Fig. 4, columnar (C) phase is energetically more stable and the molecular ordering of this phase shows two intense peaks. The nano-aggregated grain size of columnar (C) phase comes out to be 46.2090 nm and the smectic–G phase shows nano-aggregated grain sizes of the molecules are of 43.2139 nm [40, 41].

Conclusions

Optical microscopic investigations of binary mixture of dye and abietic acid molecules clearly show the molecular ordering of co-existent biphasic regions of nematic (N+I) and columnar smectic (C + I) phases for lower and higher concentrations of binary mixture of given molecule, respectively, at different temperatures. Changes in the values of electrical conductivity with temperature suggest that the grain size of aggregated molecules goes on increasing and the electrical conductivity is also increasing, while the mixture is cooled from the isotropic phase. X-ray studies lend support to found the nano-aggregated grain sizes of different liquid crystalline phases are at different temperature.

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