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Reentrant lyotropic nematic phase in a ternary mixture

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ABSTRACT

We report the results of our studies on optical and thermal properties of ternary mixture of three compounds viz., 4′-n-octyl-4-cyanobiphenyl (8CB), didodecyl dimethyl ammonium bromide, and glacial acetic acid. Higher concentrations of the given mixture show a very interesting reentrant nematic phase, sequentially when the specimen is cooled from its isotropic melt at different temperatures. The temperature variations of optical anisotropy, optical textures, and electrical conductivity have also been discussed. Nanoaggregated size of the molecules has been confirmed by X-ray studies.

KEYWORDS

Molecular orientation; optical anisotropy; phase transition; reentrant nematic

Introduction

A crystalline solid has an internal order and its elements are arranged regularly according to geometrical rules. Apart from the geometrical order there may occur an orientational order in solids. Both geometrical order and the orientational order are of long-range type and they are many times larger than the sizes of crystal lattice components. Solids are occurring in the form of monocrystals and polycrystals. A polycrystalline aggregate consists of microscopic-size crystals larger than 1 μm. The characteristic feature of the crystals is cracking along certain directions. Other properties of crystals also depend on their orientation, i.e., they exhibit anisotropy.

Liquid crystals are an intermediate state between the crystalline solids and an amorphous liquid. Therefore, it is more accurate to call them mesophases or intermediate phases. They are stable from the point of view of thermodynamics. They exhibit a long-range order and anisotropic properties of solid. Liquid crystals can be divided into thermotropic and lyotropic. The subject of interest in this paper is lyotropic liquid crystals [1, 2].

The structures of lyotropic liquid crystals are micelles, which consist of monomers whose structure differs from spherical symmetry. The shape of micelles depends both on the structure of molecules, solvent properties, concentration in solution, and the presence of other solution constituents. The ordering of micelles may lead to various spatial and orientational structures. Therefore, it can be stated that lyotropic mesophases are formed as a result of an interaction with a solvent and this process can also be affected by temperature [3–8].

In the present study, we have considered three compounds viz., 4′-*n*-octyl-4-cyanobiphenyl (8CB), didodecyl dimethyl ammonium bromide (DDAB) and glacial acetic acid (GAA). The

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polymorphic smectic modifications of the different liquid crystalline phases were observed using microscopic technique and they have been characterized by the results of X-ray and optical anisotropic techniques.

Experimental studies

The compounds 8CB, DDAB, and GAA used in this investigation were obtained from the Basic Pharma Life Science, Pvt. Ltd., India. They were further purified twice by recrystallization in benzene. The melting point of the purified sample is in good agreement with the reported value. The mixture of 18 different concentrations of 8CB in (DDAB+GAA) were prepared and kept in desiccators for a long time. Phase transition temperatures of the mixture with different concentrations were measured using Leitz-polarizing microscope and conventional hot stage. The sample was sandwiched between the slide and cover slip, which was sealed for microscopic observation. The DSC thermograms were taken for different concentrations of the mixture using the Perkin-Elmer DSC II Instrument facility available at Raman Research Institute, Bangalore, India. The X-ray diffraction studies were undertaken by using JEOL-X-ray diffractometer. The density and refractive indices of the mixtures were measured at different temperatures employing the technique as described earlier [9].

Results and discussion

Phase diagram

The partial phase diagram is as presented in Fig. 1 in the mixture of 8CB in (DDAB+GAA). This is plotted by considering the phase transition temperatures against the concentrations of the given mixture. Here, partial phase diagram shows a very interesting schlieren texture of lyotropic nematic, smectic-A, reentrant nematic, and smectic-G phases, respectively, at different temperatures. The phase diagram clearly indicates that the mesomorphism of the mixture is thermodynamically stable for all concentrations of 8CB in (DDAB+GAA). In our experimental studies, the different liquid crystalline phases have been identified on the basis of microscopic texture. These observations clearly indicate that the given mixture exhibits a very

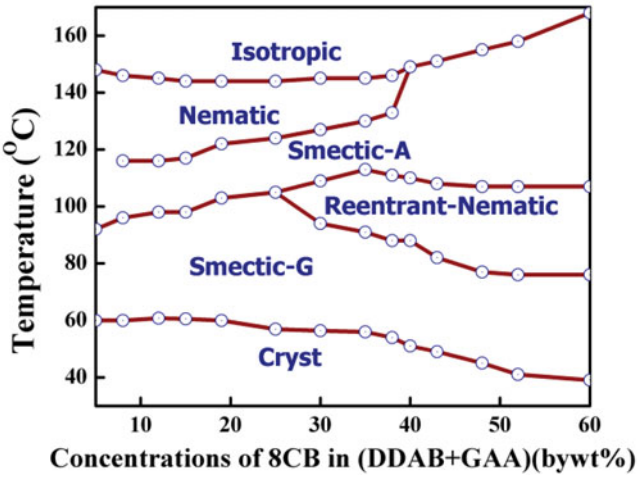

Figure 1. Partial phase diagram for the mixture of 8CB in (DDAB+GAA).

interesting reentrant nematic phase [10]. Reentrant mesophases are most commonly observed when the molecules have strong longitudinal dipole moments. The sequences of reentrant mesophases have also been found in binary mixtures of nonpolar liquid crystalline compounds [11]. The given mixture for some of higher concentrations of 8CB in (DDAB+GAA) at lower temperatures did not show the molecular aggregates in preferred direction of alignment toward the crystalline phase, but is randomly oriented to form a reentrant nematic phase. The mixture with lower concentrations of 8CB did not show the reentrant phase, but the mixture with concentrations from 25% to 60% of 8CB in (DDAB+GAA) showed a reentrant nematic phase, respectively, at different temperatures.

Optical texture studies

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. The ternary mixture with concentrations from 5% to 60% of 8CB in DDAB+GAA have been considered for the experimental studies. When the specimen of 35% 8CB in (DDAB+GAA) is cooled from isotropic liquid phase, it exhibits I–N–SmA– RN–SmG–K phases sequentially. While the sample is cooled from isotropic liquid phase, the genesis of nucleation starts in the form of small bubbles growing radially, which are identified as nematic drops. The nematic drops change over to schlieren texture of lyotropic nematic (N_D) phase as shown in Fig. 2(a) at temperature 139°C. On further cooling the specimen, the schlieren texture of N_D phase changes over to lamellar (L) smectic phase, which is characterized by the focal-conic fan texture of SmA phase and is shown in Fig. 2(b) at temperature 120°C. This phase appears to be metastable and undergoes slow transformations to give a lower temperature nematic phase and has been termed as the reentrant nematic phase. This reentrant nematic phase changes over to a broken banded focal-conic fan texture of chiral SmG phase as shown in Fig. 2(c) at temperature 80°C. If the constituent molecules of the materials, which exhibits a SmG phase, are of a chiral nature, then the phase itself may also be weakly optically active; it is then termed as a chiral SmG phase [12]. The structural studies have been carried out at that time on chiral SmG phases and it was originally simply presumed that the structure of the phase is similar to that of chiral SmC, SmI, and SmF phases. In this case, the molecules would be hexagonally closely packed in layers within each of which tilts are in the same direction. In the layer above and below, the tilt direction will, however, be turned through a small angle. Thus, on passing from layer to layer, the tilt direction will turn slowly either in an anticlockwise or a clockwise direction, depending upon the sign of the optical asymmetry of the system, and this would give a helical change in the tilt direction [13] and the same texture is retained up to room temperature. Whereas, the mixture with concentrations from 5% to 25% of 8CB exhibit a nematic phase and this phase appears to be unstable, and finally changes over from SmA to SmG phase The phase transition between a liquid crystal nematic phase (which has orientational order) and its smectic phase (which has both orientational and positional order) has long been studied for subtle effects that arise from the intrinsic coupling of their order parameters [14].

Study of refractive indices

Liquid crystals demonstrate a nonlinear response and are sensitive to their optical environments. Many of nonlinear mechanisms have revealed the promising character of these materials. The difference in refractive indices measured along perpendicular to the director axis

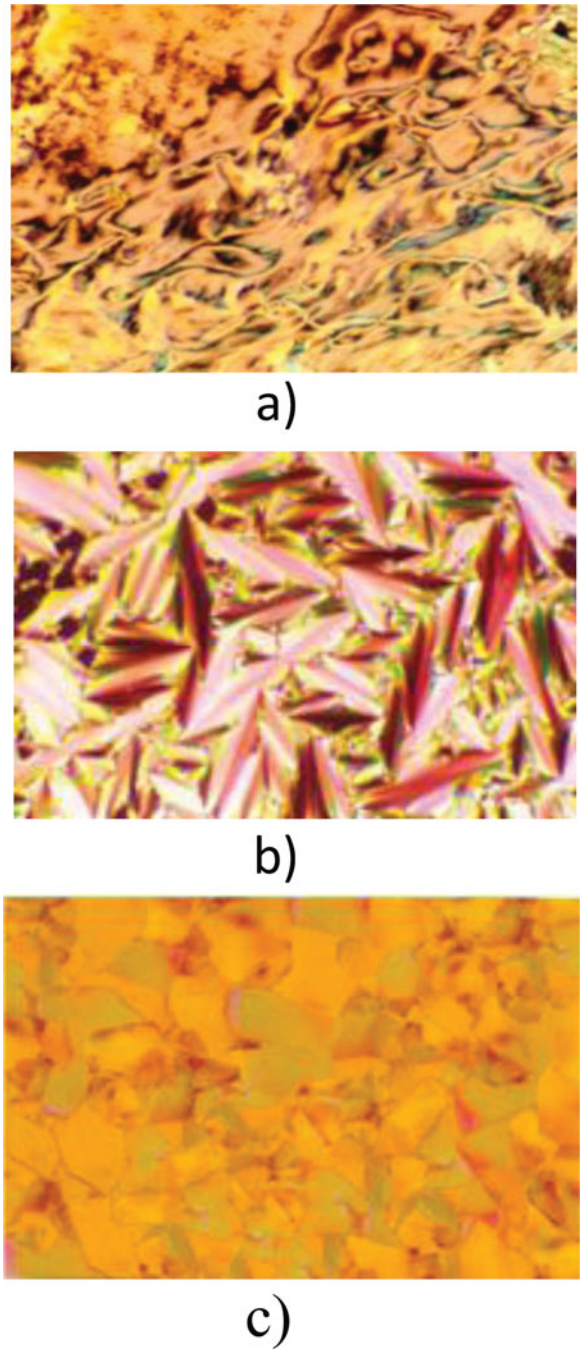

Figure 2. Microphotographs showing. a) Schlieren texture of lyotropic nematic phase (180X). b) Focal-conic, fan-shaped texture of SmA phase (180X). c) Broken banded focal-conic, fan texture of chiral SmG phase (180X).

brings the property of birefringence from the visible to the infrared region. This property provides an opportunity for various potential applications [15]. Director axis reorientation-based effects causing a change of refractive index and observations of several interesting dynamic and storage wave-mixing effects have also been extensively studied [15–17].

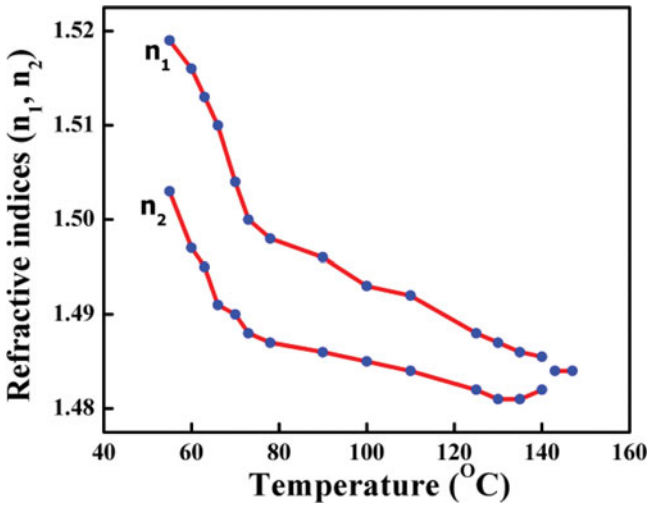

Figure 3. Temperature variations of refractive indices for the mixture of 35% 8CB in (DDAB+GAA).

The present investigations 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 the different concentrations using Abbe Refractometer and Precision Goniometer Spectrometer. The temperature variation of refractive indices for the mixture of 35% of 8CB in (DDAB+GAA) is shown in Fig. 3. From this figure it has been found that the mixture with small amount of 8CB molecule, which increases the required threshold of molecular orientation. This phenomenon demonstrates the potential application in areas such as holographic data storage. Birefringence property and its dependency on molecular orientation play an important role in understanding the molecular mechanism. Moreover, birefringence enhancement is of primary importance for the innovation of different electro-optic applications [18,19].

Conductivity measurements

Electrical conductivity measurements help in getting better idea on the phase behavior with temperature. An abrupt increase or decrease of electrica conductivity with temperature relates to the phase behavior of the lyotropic and thermotropic systems [20]. The temperature variations of electrical conductivity are shown in Fig. 4, which clearly illustrates that there is some change in the value of electrical conductivity from 56°C to 145°C, while cooling from isotropic phase for the mixture of 35% of 8CB in (DDAB+GAA). For the mixture of 35% of 8CB in (DDAB+GAA), the sequence of phase changes from lyotropic nematic-SmA-Reentrant Nematic-SmG phases. Here it has been found that the electrical conductivity goes on increasing as the temperature decreases. This suggests that aggregated molecular size starts to grow with decrease in temperature and the system slowly moves toward more orderliness [21,22].

Characterization of nanoaggregated grains

The X-ray diffractometer traces obtained for the mixture of 35% of 8CB in (DDAB+GAA) at temperature 70°C is shown in Fig. 5. The diffraction peaks at this temperature correspond to smectic-G phase (by using JEOL diffractometer with the settings: TC4, CPS400, channel width 100 for $\lambda = 1.934$ Å).

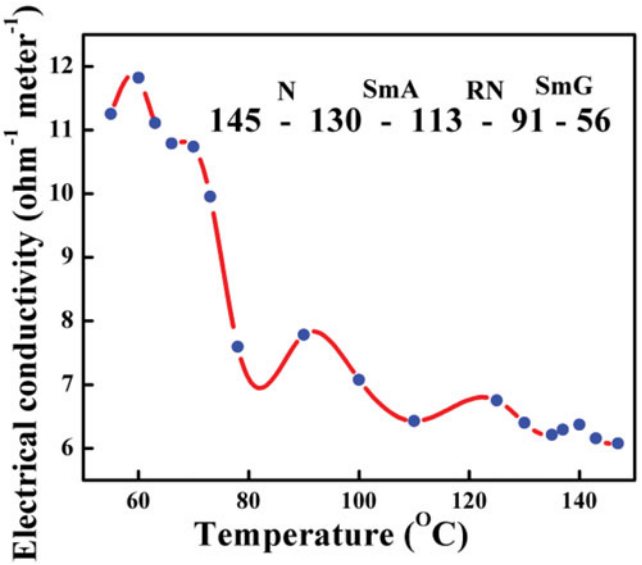

Figure 4. Temperature variation of electrical conductivity σ (Ω^{-1} m^{-1}) for the sample of 35% 8CB in (DDAB+GAA).

X-ray diffraction study is an important method to determine the nanoaggregated size of the molecules for different liquid crystalline phases [23, 24]. The X-ray traces obtained for the 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 nanoaggregated size of the molecules for different liquid crystalline phases corresponding to broadening of X-ray diffraction peaks, we have used the 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 temperature increases as it moves from crystalline phase to amorphous region [25,

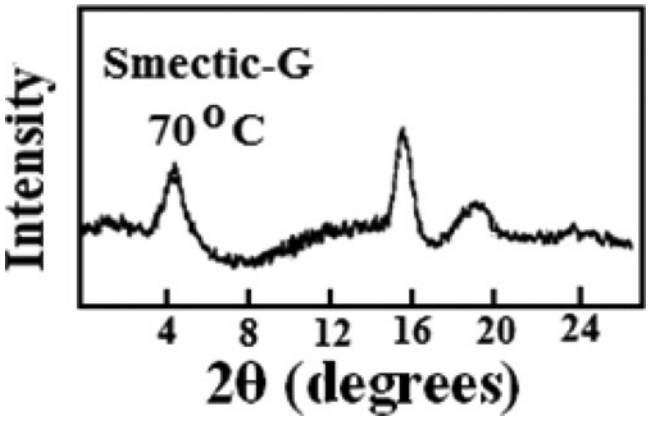

Figure 5. X-ray broadening spectrum for the mixture of 35% of 8CB in (DDAB+GAA) at 70°C temperature of smectic-G phase.

26], which clearly illustrates that, nanoaggregated size of the phase transition behavior of the molecules decreases with increasing the temperature. In Fig. 5, if we have observed that, the structure of molecular orientation for broken banded focal-conic fan texture of smectic-G phase is energetically more stable, molecular ordering of this phase shows three peaks. The nanoaggregated size of liquid crystalline material for smectic-G phase comes out to be 49.3581 nm. From this study, we have observed that the phase transition behavior of molecular ordering of the liquid crystalline materials is increasing as we move toward lower temperature. This clearly illustrates that nanoaggregated size of liquid crystalline materials of different phases are big enough to indicate that the molecular ordering [27] of layer structure increases with decrease in the temperature.

Conclusions

Optical microscopic investigations of ternary mixture of 8CB in (DDAB+GAA) molecules clearly show the molecular ordering of nematic, SmA, reentrant nematic, and SmG phases for lower and higher concentrations of given molecule, respectively, at different temperatures. Changes in the values of electrical conductivity with temperature suggest that the 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 find the nanoaggregated size of the molecules of liquid crystalline materials for smectic-G phase.

Acknowledgments

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