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Study of nano aggregates in smectic-G phase

T.N.Govindaiah, H.R.Sreepad*

Post-Graduate Department of Physics, Government College (Autonomous), Mandya-571401, (INDIA)

Email: tngovi.phy@gmail.com; hrsreepad@gmail.com

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 (DDAB) and Glacial acetic acid (GAA). 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. Nano aggregated size of the molecules has been confirmed by X-ray studies. © 2014 Trade Science Inc. - INDIA

KEYWORDS

Nano-aggregates;
Reentrant nematic;
Phase transition;
Molecular orientation;
Optical anisotropy.

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 poly-crystalline 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 polymorphic smectic modifications of the different liquid crystalline phases were observed using microscopic technique and they

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have been characterized by the results of X-ray and optical anisotropic techniques.

EXPERIMENTAL STUDIES

The compounds 4'-n-octyl-4-cyanobiphenyl (8CB), Didodecyl dimethyl ammonium bromide (DDAB) and Glacial acetic acid (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 eighteen 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 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 Figure 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 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

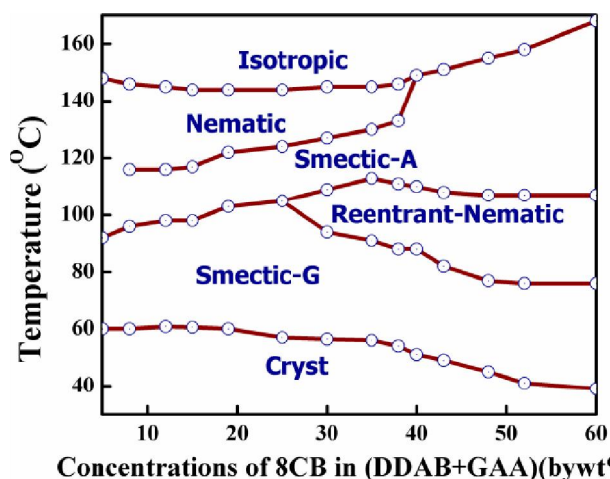


Figure 1: Partial phase diagram for the mixture of 8CB in (DDAB+GAA)

non polar 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 towards 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 Figure 2(a) at temperature 139 °C. On further cooling the specimen, the schlieren texture of lyotropic nematic (N_D) phase changes over to lamellar (L) smectic phase, which is characterized by the focal conic



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 Sm G phase (180X)

fan texture of SmA phase and is shown in Figure 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 Figure 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 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].

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 Figure 3. 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

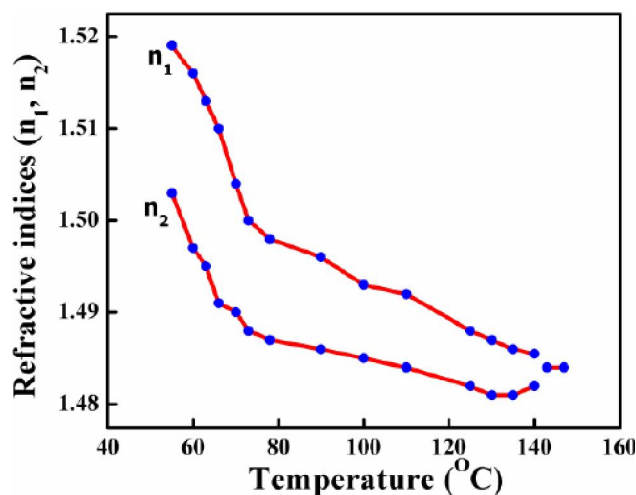


Figure 3 : Temperature variations of refractive indices for the mixture of 35% 8CB in (DDAB+GAA)

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applications^[18-22].

Characterization of nano aggregation

The X-ray diffractometer traces obtained for the mixture of 35% of 8CB in (DDAB+GAA) at temperature 70°C is shown in Figure 4. The diffraction peaks at this temperature correspond to smectic-G phase (by using JEOL diffractometer with the settings: TC4, CPS400, channel width 100 for $\lambda = 1.934 \text{ \AA}$).

X-ray diffraction study is an important method to determine the nano aggregated 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 nano aggregated 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 \AA), 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^[25,26], which clearly illustrates that, nano aggregated size of the phase transition behavior of the molecules decreases with increasing the temperature. In Figure 4, 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, mo-

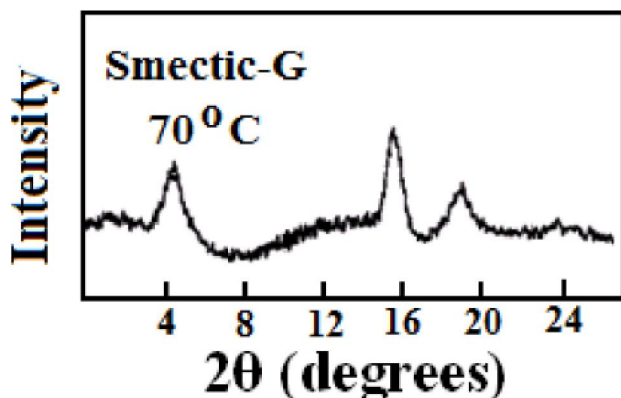


Figure 4 : X-ray broadening spectrum for the mixture of 35% of 8CB in (DDAB+GAA) at 70 °C temperature of smectic-G phase

lecular ordering of this phase shows intense three peaks. The nano aggregated 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 towards lower temperature. This clearly illustrates that, nano aggregated 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 nano aggregated size of the molecules of liquid crystalline materials for smectic-G phase.

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