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Optical and thermodynamic studies on lyotropic nematic phase in a binary mixture of liquid crystalline materials

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ABSTRACT

We report the results of our studies on optical and thermal properties of binary mixture of compounds, viz., tetradecyl trimethyl ammonium bromide (TTAB) and glacial acetic acid (GAA). The mixture exhibits very interesting schilieren texture of micellar nematic lyophase, smectic A (SmA), and SmG phases for all concentrations of TTAB sequentially when the specimen is cooled from its isotropic phase. The temperature variation of optical-birefringence has been discussed. Thermodynamic studies have also been discussed to understand the phase stability, chemical structure and molecular dynamics of the binary mixture of liquid crystalline materials.

KEYWORDS

Binary mixture;
Optical studies;
Birefringence;
Thermodynamical studies;
Molecular segregation:

INTRODUCTION

It is very interesting to study the binary and ternary mixture of some nonmesogenic compounds, which exhibit lyotropic and thermotropic mesophases[1, 2]. The lyotropic micellar nematic phase was observed by Lawson and Flautt[3, 4] in the mixture of higher concentrations of some surfactant solutions of isometric micelles, which possess long-range orientational order[5]. The micellar nematic phase was identified on the basis of microscopic texture and the fact that they spontaneously orient in a strong magnetic field. The nematic phases of disc-shaped micelles N_D and cylindrical micelles N_C occur in some lyotropic systems.

The nematic phases of disc (N_D) and cylindrical (N_C) shaped micelles have been observed by earlier investigators in a lyotropic system of mixtures. For example, a cesium pentadecafluoro octanoate (CSPFO)/water systems[6] exhibit a nematic phase (N_D), which occurs between lamellar (L) phase and isotropic micellar solution[7]. Occasionally, the phase transition of lyotropic systems exhibits isotropic, micellar nematic and lamellar phases sequentially when the specimen is cooled from isotropic liquid phase. Generally, the lyotropic phase transitions I-N_D-L correspond to isotropic (I)-nematic (N)-smectic A (SmA), exhibited by rod-shaped molecules. A similar correspondence symmetry exists between the phase involved in the lyotropic I-N_C-H transitions (H=hexagonal phase) and those in the thermotropic I-N_C-L transitions exhibited by disc-shaped molecules.

In the present investigation, we have shown the existence of micellar nematic phase, SmA and SmG phases in the binary mixture of tetradecyl trimethyl ammonium bromide (TTAB) and glacial acetic acid

(GAA). Here we have discussed results of optical texture; birefringence and thermodynamical studies have been discussed. In light of the above investigations, we have tried to understand the coupling between aggregate structure and the mesophase order.

EXPERIMENTAL STUDIES

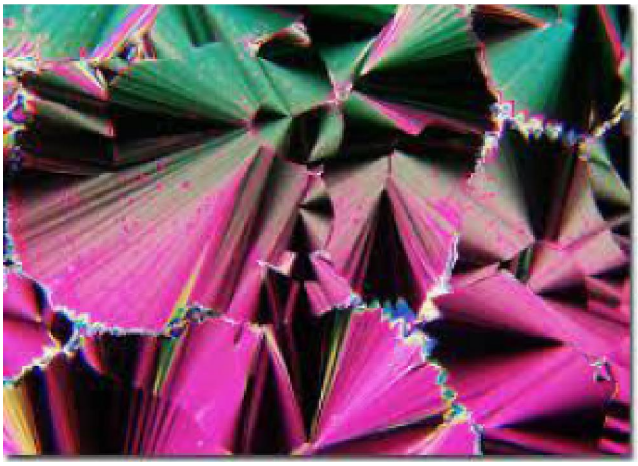
The compound TTAB used in this investigation was obtained from the Basic Pharma Life Science Pvt., Ltd., India, and it was further purified twice by a recrystallization method using benzene as a solvent. GAA was supplied from Kodak, Ltd., Kodak house, Mumbai, India. Mixtures of 25 different concentrations of TTAB in GAA were prepared and were mixed thoroughly. These concentrations of the mixture 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 sample whose refractive indices have to be determined is introduced between two prisms of the Abbe refractometer. The combination of prisms containing liquid crystalline material is illuminated by a monochromatic light (λ=5893Å). 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.

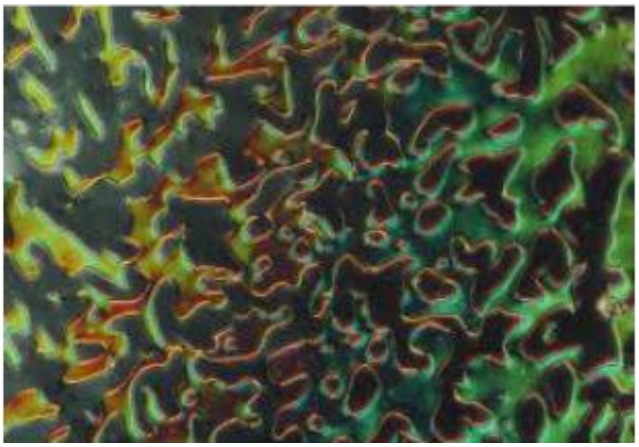
Measured refractive indices of mixtures using Abbe refractometer are compared with the results obtained by measurement using goniometer spectrometer developed by Chatelain[8]. The density and refractive indices in the optical region are determined at different temperatures by employing the techniques described by the earlier investigators[9, 10].

OPTICAL TEXTURE STUDIES

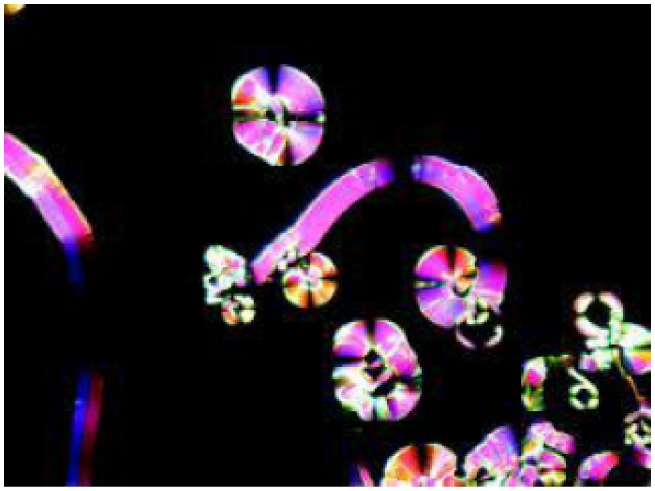
The optical textures exhibited by the samples were observed and recorded using the Leitz polarizing microscope and specially constructed hot stage. The specimen was taken in the form of thin film and sandwiched between the slide and cover glass. The concentrations from 10% to 90% of binary mixture of TTAB and GAA have been considered for the experimental studies. When the specimen of 45% TTAB is cooled from isotropic liquid phase, it exhibits I-N_D-SmA-SmG-Cryst 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, as shown in Figure 1(a). The nematic drops change over to Schlieren texture, which is the characteristic of micellar nematic phase. This is shown in Figure 1(b). On further cooling the specimen, the micellar nematic (N_D) phase changes over to lamellar (L) phase, which is characterized by the focal conic fan texture of SmA phase and is shown in Figure 1(c). Before crystallizing the specimen, SmA phase changes over to a broken banded focal conic fan texture of chiral SmG phase, as shown in Figure 1(d). 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[11]. 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 must be 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[12] and the same texture is retained up to room temperature. Whereas the concentrations from 10% to 90% of TTAB exhibit a micellar nematic phase and this phase appears to be stable, and



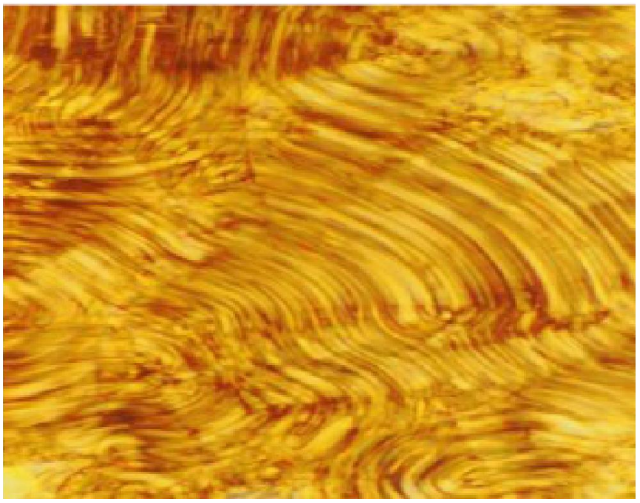
Lyotropic micellar nematic drops



Focal conic fan shaped texture of smectic-A phase



Schlieren texture of lyotropic micellar nematic phase



Broken banded focal conic fan texture of chiral SmG phase

Figure 1 : Microphotographs obtained in between the crossed polars.

finally changes over from SmA to SmG phase. The micellar nematic phase has a long-range orientation order and the micelles are arranged in columns. Similar micellar nematic phase has been reported by our group in themixture of N-Cetyl-N, N, N, trimethyl ammonium bromide, and GAA[13].

OPTICAL ANISOTROPY

Results of this investigation are further supported by the optical studies. We have measured the temperature variation of the refractive indices (n_e and n_o) for the mixture of different concentrations of TTAB and GAA by using Abbe refractometer and precision goniometer spectrometer using the wavelength 589.3 nm in the lyotropic nematic and lamellar smectic phases. The refractive index n_e due to extraordinary ray and n_o due to ordinary ray have been determined. The temperature variations of birefringenec for 45% of TTAB in GAA are shown in Figure 2. From the figure, it can be observed that wherever there is an isotropic–liquid crystalline phase transition, the value of birefringence changes appreciably, which indicates that the changes correspond to various smectic modifications. Further, with increase in the concentration of TTAB, the value of birefringence decreases with temperature because the effective optical anisotropy associated with the molecules of TTAB also decreases[14, 15].

THEMODYNAMIC STUDIES

Studies on different mixtures of liquid crystalline materials are more important not only from the

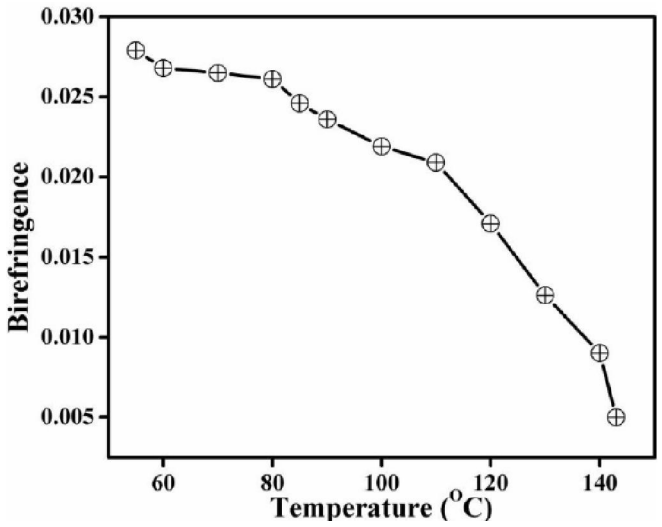


Figure 2 : Temperature variations of birefringence for the sample of 45% TTAB in GAA

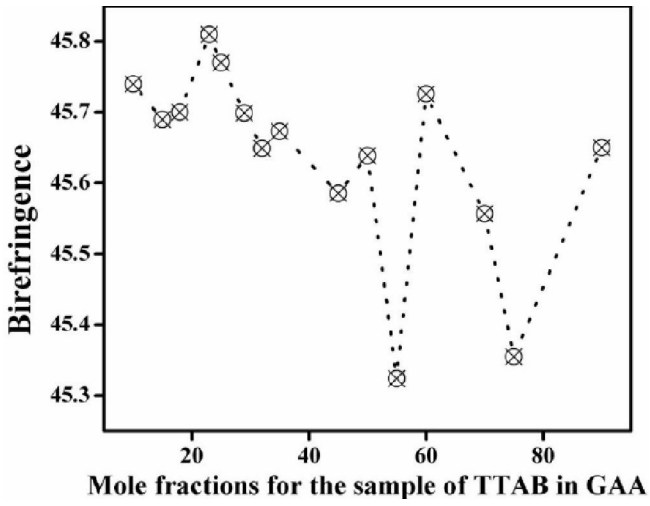


Figure 3 : Variations of birefringence as function of mole fraction for the sample of TTAB in GAA

viewpoint of their technological applications but also from that of fundamental studies in the field of molecular interactions[16]. Thermodynamic studies are very important role to understand the phase stability, chemical structure and dynamics of liquid crystals[17, 18]. Temperature dependent molecular orientations of liquid crystalline phases have been considered in many technological applications. The applied applications of these technologies are based on the properties of molecular structure and intermolecular interactions. The intermolecular forces such as van der Waals interaction, hydrogen bonds, electron donor interactions and steric repulsive interactions are they individually or together may be responsible for increasing or decreasing the thermal stability of liquid crystalline phase[19]. Thermodynamical variations of liquid crystalline phase at different concentrations of binary mixtures of liquid crystalline materials are estimated using Boltzmann distribution laws. Draw a graph of variations of birefringenc as a function of mole fraction for the sample of TTAB in GAA at constant temperature 88 ^{0}C is presented in Figure 3, which clearly shows, the degree of microphase separations are one of the parameters to controlling a physical properties of liquid crystalline materials[20]. In this context the existence parameter can be varied infinitesimally small either through chemical modification or through physical modification and hence they are depends on nature of additives molecules. The figure clearly illustrates that, statistically how the molecular interactions are thermodynamically changes at different concentrations in order to show the thermal stability of liquid crystalline phase. Here we noticed that: at constant temperature the given molecules are fractionally varies as increasing the concentrations of the additive molecules. In this study it is very interesting to observe the spin temperature. Due to this temperature on the molecular surface the internal degrees of freedom of the molecules are thermodynamically equilibrium with one mole fraction to the other mole fractions. If either increasing or decreasing the mole fraction; which cause a small variation of electrostatic potentials and which they around the molecule. In spite of these uncertainties, the full set of partial charges is very useful, as it can provide a detailed insight into the molecular arrangement in mesophases and they reproduce the electrostatic potential very well. The molecular density of mesosphere, charges on molecules represent an electrostatic molecular interaction, but they do not show the real charge distribution in molecule. The molecular ordering or the phase stability of liquid crystalline phase at given constant temperature: the intermolecular interactions are responsible for the charges of carbon and the adjacent hydrogen molecules and which shows the correct electrostatic potentials are reproduced by different partial charge distributions.

CONCLUSIONS

The salient features of this investigation are the following: The existence of micellar nematic phase, SmA and SmG phases have been observed by using microscopic technique in binary mixture of TTAB in GAA. The drastic changes in the value of birefringence with the variation of temperature unambiguously correspond to smectic and micellar nematic phases. Thermodynamic studies have also been discussed to understand the phase stability, chemical structure and molecular dynamics of the binary mixture of liquid crystalline materials.

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