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RESEARCH ARTICLE

OPTICAL AND THERMODYNAMICAL RESPONSE OF ORDER PARAMETER OF REENTRANT NEMATIC PHASE IN A TERNARY MIXTURE OF LIQUID CRYSTALLINE MATERIALS

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ABSTRACT

We report the results of our studies on the optical and thermal properties of multi-component systems namely, laurylpyridinium chloride (LPC), 4-cyano-4′-octyloxybiphenyl (8OCB) and Glacial acetic acid (GAA), which exhibits a very interesting lower temperature reentrant nematic and reentrant smectic-A phases, sequentially when the specimen is cooled from its isotropic liquid phase. The order parameter (S) of the reentant lyotropic nematic (ReN_D) phase is estimated with the help of temperature dependence of optical anisotropy from the measured values refractive index and density data. The temperature variation of order parameter of the experimental curve is very well fitted with the Mayer-Saupe theoretical curve. Thermodynamical response of order parameter of reentant lyotropic nematic (ReN_D) has also been discussed to understand the stability of liquid crystalline phase, chemical structure and molecular dynamics of the given mixture.

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INTRODUCTION

Reentrant behavior in liquid crystals was first discovered by Cladis (1975). Successive nematic (N), smectic A and reentrant nematic phases as a function of decreasing temperature could be produced either by pressure in a single material (Cladis *et al.,* 1978) or by making appropriate mixtures of materials with and without smectic A phases. Since this seminal work, a large number of materials and mixtures have been discovered which exhibit reentrant phenomena. These materials possess common features: that the constituent liquid crystalline molecules have strongly polar end groups. In a series of beautiful experiments the Bordeaux group and others have shown that these polar materials exhibit unexpectedly rich behavior with at least six distinct smectic A or C phases (Johnson *et al.,* 2014; Guillon *et al.,* 1978; Kalkura *et al.,* 1983). The reentrant phenomenon must ultimately be understood within this broader context. Reentrant behavior at first seems to violate the intuitive notion that less ordered phases should exist at higher temperatures than high symmetry ones. In fact, however, reentrancy is observed in a broad range of physical systems. Examples include reentrant behavior in magnetic superconductors, reentrant spin glass. Behavior in mixtures of ferromagnet and antiferromagnets (Harris *et al.,* 1999), and reentrant melting in surface monolayers exhibiting commensurate and incommensurate periods (Aeppli *et al.,* 1983). This final example is particularly germane to the liquid crystal problem. In all of these cases the phase transition return to a disordered state with decreasing temperature is caused by competing order parameters. It is likely that competing order parameters account for the Nematic-Smectic-A-Reentrant Nematic behavior in the polar liquid crystal systems. However, because of our rather poor understanding of the microscopic interactions responsible for smectic ordering in the first place, it is not obvious what is the appropriate choice of order parameters. Further, predictive theory turns out to be quite difficult. Early theories (Cladis *et al.,* 1978), inspired by the bilayer nature of the A phase, introduced the degree of pairing as an order parameter. This has been elaborated on by Longa and de Jeu (Moncton *et al.,* 1981). Others have included the dipole moment (Longa and De jeu, 1982; Berker and Walker, 1981) as the additional order parameter. An alternative

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approach, based on the concept of an optimal density for smectic ordering, has been given by Pershan and Prost (Nagabushan, 1988). Unfortunately, these theories are all primarily qualitative in character although by appropriate measurements it is possible to show that certain of them are highly implausible. In the present investigation, we have shown the existence of Lyotropic Nematic (N_D), Smectic-A (SmA), Reentant lyotropic nematic (ReN_D), Reentant Smectic-A and smectic-G (SmG) phases, respectively, at different concentrations in the ternary mixture of laurylpyridinium chloride (LPC), 4-cyano-4′-octyloxybiphenyl (8OCB) and Glacial acetic acid (GAA). 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 aggregated structure and the mesophase order in light of the observations regarding reentant lyotropic nematic (ReN_D) and reentant Smectic-A (Pershan and Prost, 1979), wherein it has been observed that, the aggregates formed at low concentrations are large enough to align and also as we increase on at higher concentrations, the aggregated size decreases. The thermodynamical response of order parameter of reentant lyotropic nematic (ReN_D) has been discussed.

Experimental studies

In the present study, we use the materials, namely, laurylpyridinium chloride (LPC), 4-cyano-4′-octyloxybiphenyl (8OCB) and Glacial acetic acid (GAA). Mixtures of different concentrations of GAA in (LPC +8OCB) were prepared and they were mixed thoroughly. These mixtures of concentrations were kept in desiccators for 6 hours. Samples were subjected to several cycles of heating, stirring, and centrifuging to ensure homogeneity. Phase transition temperatures of these mixtures 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 density and refractive indices in the optical region are determined at different temperatures by employing the techniques described by the earlier investigators (Govindaiah *et al.,* 2015; Nagappa *et al.,* 1983; Goldar *et al.,* 2007).

RESULTS AND DISCUSSION

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 of GAA in (LPC +8OCB) exhibits different liquid crystalline phases and the phase transition temperatures are measured by using Leitz-polarizing microscope. The partial phase diagram is as shown in Figure 1. This is obtained by plotting the concentrations against the phase transition temperatures of the mixture. The phase behavior is discussed with the help of phase diagram. The concentrations from 5% to 45% of ternary mixture of GAA in (LPC+8OCB) have been considered for the experimental studies. When the specimen of 15% GAA is cooled from isotropic liquid phase, it exhibits I–N_D–SmA–ReN_D–ReSmA–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 schlieren texture of nematic phase as shown in Figure 2(a).

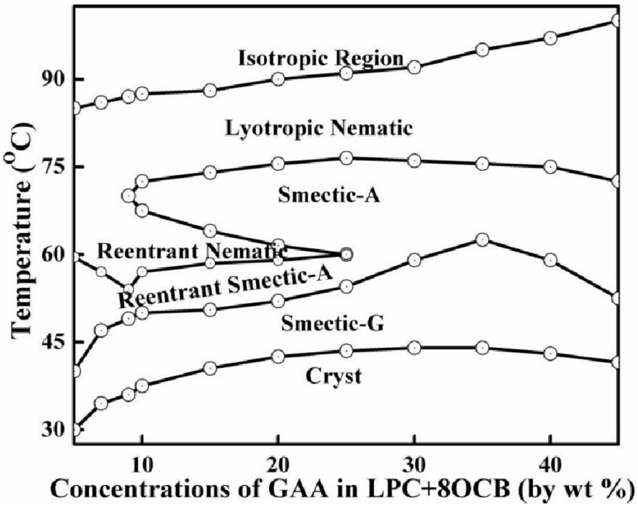
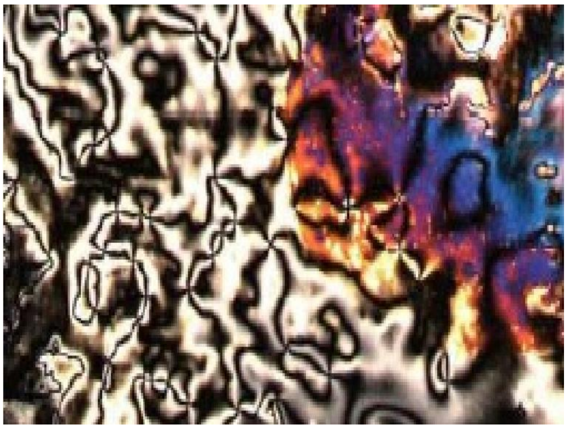
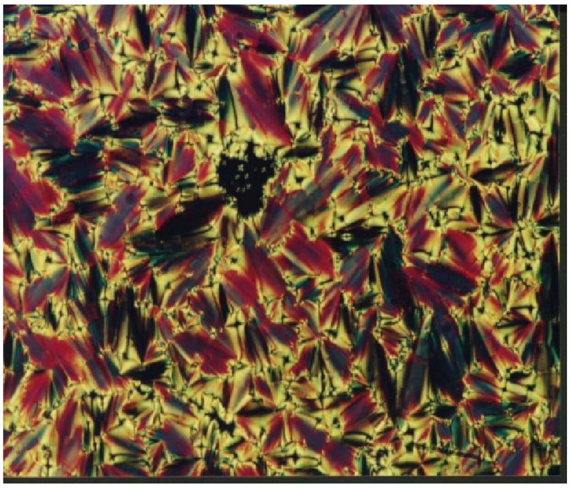


Figure 1. Partial phase diagram for the mixture of GAA in LPC+8OCB



a). Schlieren texture of lyotropic nematic (N_D) phase.



b). Focal conic fan texture of Smectic-A phase (250X).

Figure 2. Microphotographs obtained in between the crossed polars,

On further cooling the specimen, the schlieren texture of lyptropic nematic (N_D) phase changes over to lamellar (L) phase, which is characterized by the focal conic fan texture of SmA phase and this phase is shown in Figure 2(b). Then this phase appears to be metastable and undergoes slow transformations to give a thread-like texture of nematic phase, which has been termed as the lower temperature reentrant lyotropic nematic (ReN_D) phase. On further cooling the specimen, the lyotropic nematic (ReN_D) phase was slowly changed over to bubbles in the form of battonnets, which are the characteristic of SmA phase and this phase has been termed as the reentrant SmA (ReSmA) phase. Before crystallizing the specimen, the ReSmA phase slowly changes over to a broken banded focal conic fan texture of chiral SmG phase. If the constituent molecules of the materials, which exhibit an 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 (Thiem *et al.,* 1989). 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 (Leadbetter *et al.,* 1979) and the same texture is retained up to room temperature. Whereas the concentrations from 26% to 45% of GAA exhibit a lyotropic nematic (N_D) 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 (Gane *et al.,* 1981).

Birefringence studies

The micellar nematic (N_D) phase in lyotropic system is generally formed by amphiphilic aggregation with bilayer structure (Yethiraj *et al.,* 2007). As in nematic phase of thermotropic system, the bilayer micelles show some degree of parallel orientation, which is responsible for the macroscopic anisotropy of the phase. The birefringence study helps us to understand the optical anisotropic properties of the samples. The orientational order parameter of the reentrant lyotropic nematic (ReN_D) phase is essential to understand the degree of orientations of the micelles (Haven *et al.,* 1981). In the present investigation, we have measured the temperature variation of refractive indices (n_1 and n_2) and densities for the mixture with different concentrations by using Abbe refractometer and precision Goniometer spectrometer using the wavelength 5893Å in the nematic and smectic phases. Refractive indices n_1 due to extraordinary ray and n_2 due to ordinary ray have been determined. Saupe et al. (1984) have used the modified Lorentz–Lorentz (1979) formula for the calculation of orientational order parameters of the lyotropic mixture. The refractive indices n_1 and n_2 are given by:

$$\frac{n_1^2-1}{n_2^2+2}=4\frac{\pi}{3N}\left[W_{GAA}\alpha_{GAA}+W_{LPC+8OCB}\alpha_{LPC+8OCB}-\left(\frac{2}{3}\right)W_{LPC+8OCB}\Delta\alpha_{LPC+8OCB}S\right] \quad \ldots\ldots\ldots\ldots\ldots 1$$

$$\frac{n_1^2-1}{n_2^2+2}=4\frac{\pi}{3N}\left[W_{GAA}\alpha_{GAA}+W_{LPC+8OCB}\alpha_{LPC+8OCB}-\left(\frac{1}{3}\right)W_{LPC+8OCB}\Delta\alpha_{LPC+8OCB}S\right] \quad \ldots\ldots\ldots\ldots 2$$

where N is the number of molecules per unit volume of the mixtures, W_{GAA} and $W_{\mathrm{LPC+8OCB}}$ are the mole fractions of GAA and LPC+8OCB, respectively, and α is the mean polarizability of the respective compounds. For the estimation of orientational order parameter of the reentrant nematic (ReN_D) phase, we assume only the birefringence Δn of the LPC+8OCB molecules. The polarizability tensor of LPC+8OCB can be approximated with principle polarizability $\alpha_1$parallel to the long axis of the molecule and α_2 perpendicular to it. The optical anisotropy ($\Delta\alpha$) contribution from acetic acid is neglected. Therefore, only $\Delta\alpha$ of LPC+8OCB molecules is considered, $\Delta\alpha=(\alpha_1-\alpha_2)$ and $S=½(3\cos^2\theta-1)$ is the degree of order of the LPC+8OCB molecules, where θ is the angle between the long molecular axis and optic axis of the molecular disc in the reentrant lyotropic nematic (ReN_D) phase and $\cos^2\theta$ is the average over the molecular motion.

From the equations 1 and 2, and using $\Delta n = (n_e - n_o) << 1$ we obtain

$$\Delta n=\frac{\left[2\pi(n_2^2+2)^2 N\Delta\alpha W_{LPC+8OCB}S\right]}{9n_2} \quad \ldots .3$$

In order to estimate the value of optical anisotropy ($\Delta\alpha$) of LPC+8OCB molecule, the value of $(\alpha_{||})_{\mathrm{eff}}$ i.e., the polarizability along the axis of the molecules and $(\alpha_\perp)_{\mathrm{eff}}$ the polarizability perpendicular to the long axis of the molecule, the value of $(\alpha_{||})_{\mathrm{eff}}$ of each group is calculated from the optical anisotropy of bond polarizability data for the wavelength 5893 Å assuming that the molecules have all trans-configuration and hence $(\alpha_\perp)_{\mathrm{eff}}$ may also be calculated. Using the values of $(\alpha_{||})_{\mathrm{eff}}$, $(\alpha_\perp)_{\mathrm{eff}}$ and α the mean polarizability, the value of $\Delta\alpha$ is estimated (23). The value of ($\Delta\alpha$) for LPC+8OCB molecules turns out to be $43.642\mathrm{X}10^{-24}$ cm^3. The order parameter (S) of the reentant lyotropic nematic (ReN_D) phase is calculated with the help of ($\Delta\alpha$) value. The order parameter (S) value of the mixture was estimated at different temperatures for different concentrations. Boden et al. (1979) have pointed out in their study that the variation of birefringence with temperature is dependent upon both the size and shape of the micelles, in addition to their dependence on the orientational order. However, we also notice that the order parameter varies with mole percent of LPC+8OCB in the reentant lyotropic nematic (ReN_D) phase. It is observed that the order parameter (S) decreases with decreasing the concentrations of LPC+8OCB. The temperature variations of order parameter of reentant lyotropic nematic (ReN_D) phase are as shown in Figure 3, the experimental values of the order parameters are compared with the Maier-Saupe theoretical curve. It is observed that, the trend of the variation of order parameter (S) values agrees with the Maier-Saupe theoretical curve. The values of birefringence are in good agreement with the values measured using the interference techniques (Somashekar and Krishnamurti, 1981; Govindaiah *et al.,* 2012; Govindaiah, 2016).

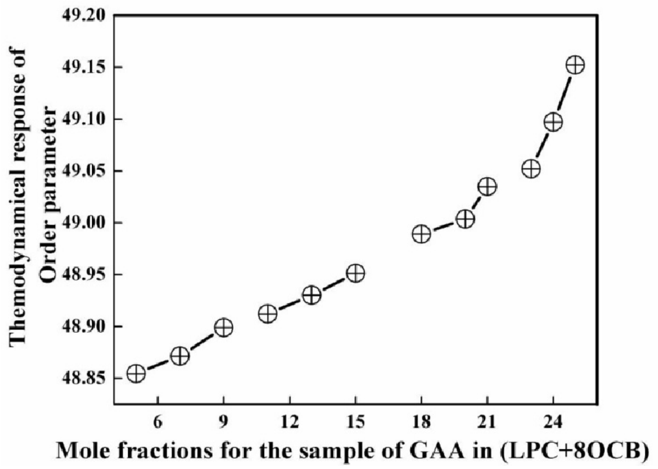


Figure 3. Temperature variations of order parameter of reentant lyotropic nematic (N_D) phase

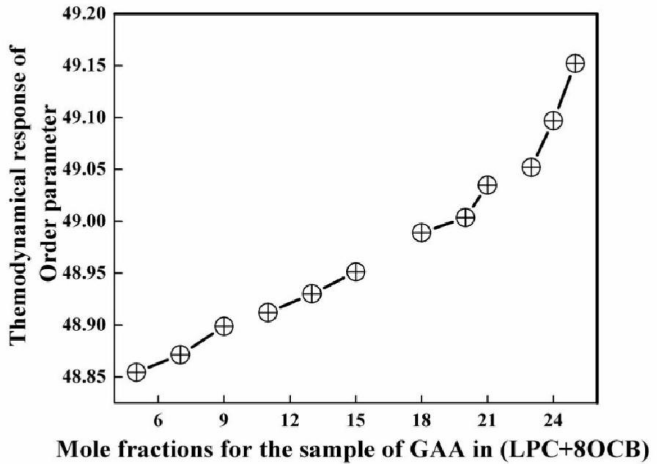


Figure 4. Thermodynamical response of order parameter as a function of mole fraction for the sample of GAA in (LPC+8OCB)

Themodynamical response of order parameter

Studies on multi-component system of liquid crystalline materials are more important not only from the viewpoint of their technological applications but also from that of fundamental studies in the field of molecular interactions (Collings and Hird, 1997). Thermodynamical response of orientational order parameter is an very important role to understand the stability of liquid crystalline phase, chemical structure and molecular orientations of liquid crystals (Soule and Rey, 2012; Amoros *et al.,* 2009). 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 (Lubensky, 2011). Thermodynamical response of orientational order parameter for reentrant lyotropic namatic ((ReN_D) phase at different concentrations of multi-component system of liquid crystalline materials are estimated using Boltzmann distribution laws. If we draw a graph of variations of thermodynamical response of order parameter of reentrant lyotropic nematic (ReN_D) phase as a function of mole fractions for the sample of GAA in (LPC+8OCB) at constant temperature 62 ^{0}C is presented in Figure 4, which clearly shows, the degree of micro molecular separations are one of the parameters to controlling a physical properties of given different liquid crystalline materials (Kercha YuYu, 1979). In this context the existence orientational order parameter of lyotropic reentrant nematic (ReN_D) can be varied either through chemical modification or through physical modification and hence they are depends on nature of additives molecules. From the figure clearly we observed that, statistically how the molecular orientations of order parameter of lyotropic reentrant nematic (ReN_D) phase is thermodynamically changes at different concentrations in order to show the thermal stability of liquid crystalline phase. Here if at constant temperature: the orientational order parameters of the given molecules are fractionally varies as increasing the concentrations of the additive molecules. In this study: it is very interesting to observe a spin temperature. Due to this gradient temperature: on the surface area of liquid crystalline lyotropic reentrant nematic (ReN_D) phase, the degrees of freedom of order parameter of the given molecules are thermodynamically varies with one mole fraction to the other. If an increasing the mole fractions for the sample of GAA in (LPC+8OCB); the value of thermodynamical response of molecular orientations of order parameter are restrained and then it varies from concentrations to concentrations and hence it also changes the intermolecular energy of given molecules with spin temperature, because the effective intermolecular interactions of anisotropic energy associated with the molecules of GAA increases with the additive ones. The molecular ordering or thermodynamical stability of lyotropic reentrant nematic (ReN_D) at given constant temperature: the intermolecular interactions of anisotropic energy are responsible for the charges of carbon and adjacent hydrogen molecules: and hence it shows the correct electrostatic potentials, which are reproduced by different partial charge distributions. If an increasing the mole fractions for the samples of GAA in (LPC+8OCB), it shows small variation of electrostatic potentials and which they around the molecule. In spite of these uncertainties, the full sets of partial charges are very essentials as it can provide a detailed insight into the molecular arrangements of the mesophase.

Conclusion

In light of the above results, we have drawn the following conclusions. Optical microscopic investigations of ternary mixture of GAA in (LPC+8OCB) clearly shows the molecular ordering of reentrant lyotropic nemtaic (ReN_D) and reentrant smectic-A phases respectively for lower concentrations and at different temperatures. The phase behavior is discussed with the help of phase diagram. Variations are observed in the values of orientational order parameter of lyotropic nematic

(ReN_D) phase are expected to due to the changes in the dimension of disks along with changes in the order of molecular arrangement. Thermodynamical response of orientational order parameters of reentrant lyotropic nemtaic (ReN_D) phase have also been discussed to understand: statistically how it thermodynamically changes at different concentrations in order to show the thermal stability, phase stability, chemical structure and molecular dynamics of the ternary mixture of liquid crystalline materials.

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