RESEARCH ARTICLE

OPTICAL, ELECTRICAL AND DIELECTRIC PROPERTIES OF MIXTURES OF LIQUID CRYSTALLINE MATERIALS

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ABSTRACT

In the present work, our investigation is to study the optical, electrical and dielectric properties of the binary mixture of cholesteryl nonanoate (CN), butoxy-benzylidene-p-n-anilino-acetophenone (BBAA), which exhibits very interesting liquid crystalline cholesteric, TGB SmA, SmC, SmB and ReSmA phases sequentially when the specimen is cooled from isotropic phase. These phases have been characterized by using microscopic and optical anisotropic techniques. The temperature variations of dielectrics and electro-optical effects have also been discussed. X-ray studies have been used to calculate the nano-aggregated grain size of the molecules.

INTRODUCTION

Liquid crystals are an attractive model system for studying mesophase ordering and phase transitions. The phase behavior of liquid crystal is strongly influenced by disorder and impurities and is easily handled allowing for unique control of the important physical parameters. Examples of induced random field-like disorder through random surface interactions are controlled porous glass and other uniform cylindrical confinements (Demus *et al*., 1998; Madhusudana, 2001; Rizvi. 2003). A typical intermolecular energy responsible for the stability of the relevant order in the medium is comparable to the thermal energy and thus liquid crystals are soft materials. Relatively weak interactions like those between molecular dipoles or chiral centers of appropriate molecules can give rise to new types of liquid crystals. The soft nature of the medium, coupled with anisotropic optical and dielectric properties gives rise to many electro-optic effects at relatively low voltages.

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These are exploited in liquid crystal displays, which are the lowest power consuming flat panel devices and used in all calculators, laptop and palmtop computers, cell phones, full-size television screens, etc. (Figueiredo Neto, 2005; Petrov, 1999; Govindaiah *et al*., 2013). In the present investigation, our aim is to study the mixture of multi-components, namely, cholesteryl nonanoate (CN), butoxy-benzylidene-p-n-anilino-acetophenone (BBAA), which exhibits liquid crystalline cholesteric, TGB and smectic phases, such as SmA, SmC and SmB phases, respectively, at different temperatures. They were observed using microscopic technique and also been verified from the results of optical anisotropic techniques. The dielectrics and electro-optical studies have also been discussed.

MATERIALS AND METHODS

In the present investigation, we have studied binary mixtures of liquid crystals, namely, cholesteryl nonanoate (CN), butoxy-benzylidene-p-n-anilino-acetophenone (BBAA) which are obtained from M/s Eastman Organic Chemicals, USA. The chemicals are purified twice with benzene. Mixtures of different concentrations of BBAA in CN were prepared and

were mixed thoroughly. These mixtures of different concentrations 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 a 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.

Dielectric measurements

The values of capacitance and dissipation factor of the sample holder with, and without sample, were determined by impedance/ gain phase analyzer of Hewlett-Packard (HP 4194A). The real part of the permittivity of the sample is obtained from the change in the capacitance value of the sample holder, due to the presence of sample, using the following equation:

$$\epsilon' = \frac{\Delta C}{C_G} + 1$$

where, ΔC, the change in the capacitance of sample holder due to the presence of sample, is

$$\Delta C = C_P - C_O$$

where, C_P is the capacitance with sample, and C_O is the capacitance without sample. C_G is the geometrical capacitance of the sample holder.

The loss tangent and dissipation factor (D) of the sample were derived from the dissipation factor and capacitance, measured for the sample holder with, and without sample, and is given by:

$$\tan\delta = \frac{C_P D_P - C_O D_O}{C_P - C_O}$$

where, D_P is the dissipation with sample, and D_O is the dissipation without sample.

The loss factor is given by the following equation

$$\epsilon'' = \epsilon' \tan\delta$$

Capacitance and dissipation factor values were recorded in the present study. The temperature of the sample was maintained by placing the sample cell on a specially designed double walled brass chamber, in which heated oil was circulating, with the help of a Julabo F-25 refrigerated circulator. It has the facility of setting the temperature of the sensor used, and so the temperature of the sample, i.e. the sensor temperature has been measured directly from the display of the monitor (Operating Manual, JULABO). The temperature was measured by placing a thermocouple in close vicinity to the sample, with an accuracy of 0.1^0C.

Electro-optical measurements

Electro optical measurements were carried out by the usual experimental setup of Williams (Williams, R. 1963). It consists

of tin oxide coated transparent conducting glass plate and the sample sandwiched between these two glass plates. Teflon spacers having thickness of d=39 ±1 μm were used and observations were made at 60 ^{0}C using polarizing microscope in conjunction with a hot stage.

RESULTS AND DISCUSSION

Phase diagram

The partial phase diagram is a very important method to determine the stability of liquid crystalline phase at different temperatures for different concentrations of the liquid crystalline materials. The partial phase diagram in the present case is as shown in Figure 1. This clearly illustrates that mixtures with the concentrations ranging from 5% to 85% of BBAA in CN exhibit cholesteric phase TGB and smectic phases, such as SmA, SmC and SmB phases sequentially when the specimen is cooled from isotropic melt. The mixtures with concentrations of BBAA ranging from 5% to 25% and 42% to 85% of Cho, SmA, SmC, ReSmA and SmB phases, concentrations ranging from above 25% and below 45% of BBAA shows an very interesting twisted grain boundary (TGB) phases respectively at different temperatures. The interesting feature of this phase diagram clearly shows an unconventional sequence of twisted grain boundary phase in addition to Cho, SmA and SmB phases in the middle concentrations of BBAA (Govindaiah, *et al*., 2015: 2013: 2015).
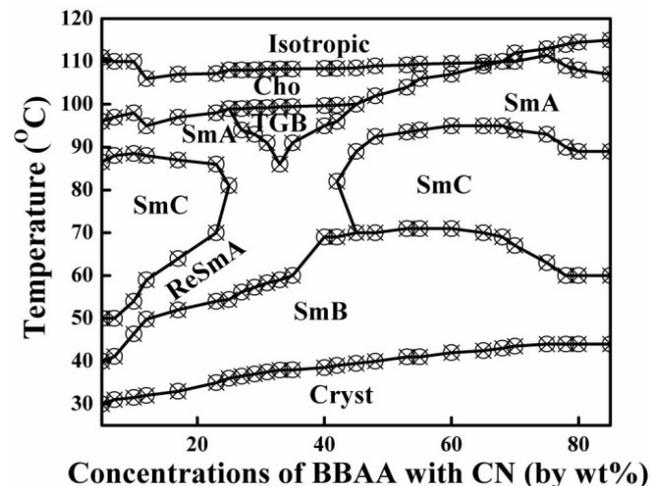
Figure 1. Partial phase diagram for the mixture of BBAA with CN

Optical texture studies

For the purpose of optical texture studies, the sample was sandwiched between a slide and a cover glass, and then the optical textures were observed using a Leitz-polarizing microscope in conjunction with a specially constructed hot stage. When molten sample of the mixture of 29% BBAA mixed with CN was cooled from its isotropic phase, nucleation starts in the form of minute bubbles and immediately the bubbles grow radially and form fingerprint pattern, which is characteristic of the cholesteric phase with large values of

pitch (Demus,D, *et al*., 1978: Nagappa, *et al*., 1983). On further decreasing the temperature of the sample, the cholesteric phase changes over to smectic phase, passing through an intermediate phase and it is assigned by the appearance of mobile thread-like textures in the homeotropic region, which is the characteristic of twisted grain boundary phase as shown in Figure 2(a). The helical axes of the twisted grain boundary phase lies in a direction parallel to the smectic layer planes (Nagappa, *et al*., 1997: Nguyen H. T, *et al*., 1992). On further cooling, the TGB phase changes over to focal conic fan shaped texture of SmA, which is shown in the Figure 2(b).

Figure 2(a). Mobile thread like filament texture of TGB phase (250X)
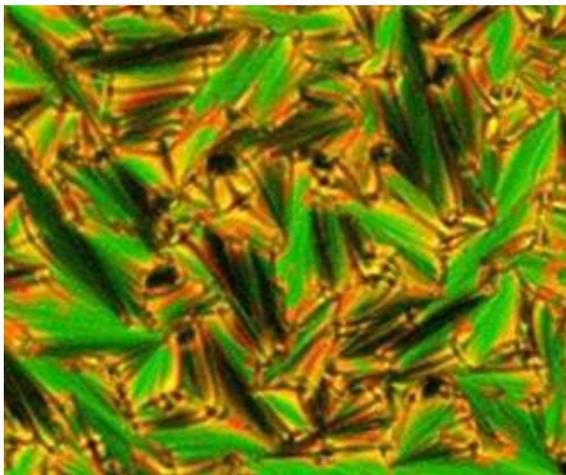
Figure 2(b). Focal conic fan shaped texture of SmA phase (250X)

Structure of molecular orientation of SmA phase is not stable at temperature 83^0C and then it changes over to broken focal conic fan-shaped texture of SmB phase respectively at different temperatures. In this system, the microscopic observations clearly indicate that the given mixture with concentrations ranging from 5% to 25% of BBAA in CN exhibits ReSmA phase (Govindaiah, *et al*., 2014). The lowest temperature mesophase of certain compounds exhibits two or more mesophases of the same type, over different temperature ranges. Re-entrant 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 non-polar liquid crystalline compounds

(Baron, M. 2001). In the given mixture, some of the middle concentrations of BBAA at lower temperatures did not show the molecular aggregates in the preferred direction of alignment towards the crystalline phase, but it randomly oriented to form a reentrant SmA phase and then this phase changes over to a broken focal conic fan-shaped texture of the SmB phase and then it becomes crystalline phase, which remains stable at room temperature [Govindaiah, *et al*., 2013: 2015).

Dielectric parameters

The dielectric studies give very useful information about molecular structure, molecular dynamics and phase transition behavior and they are used as an input to its display applications (Gharadjedaghi, F. *et al*., 1976: Hill, N. E. *et al*., 1969.). In addition; the dielectric anisotropy of the liquid crystal arising from angular correlation between the molecules, not only throw light on individual molecular structure but also their ordering in a particular mesophase, which may be characterized by order parameter. Since the value of dielectric permittivity and dielectric loss vary with the variation of temperature, these parameters can be used to measure the transition temperatures of pure liquid crystals as well as their mixtures. At a constant frequency of 5 kHz, the temperature variations of dielectric parameters such as dielectric constant (ε') and dielectric loss (ϵ'') have been measured for the mixture of 29% BBAA with CN is presented in Figure 3(a, b).
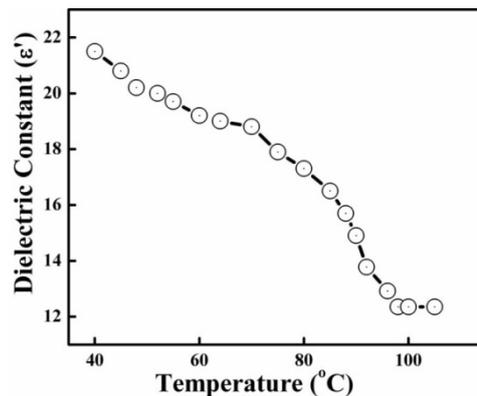
Figure 3(a). Temperature variation of dielectric constant for the sample of 29% BBAA with CN
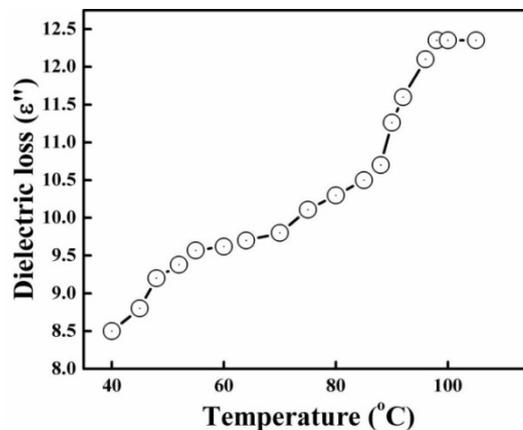
Figure 3(b). Temperature variation of dielectric loss for the sample of 29% BBAA with CN

From the figure it is clear that, the discontinuities are observed; while passing through different liquid crystalline phases, which appear from smectic-isotropic region. The dielectric parameter ϵ' decreases with increasing the temperature and the parameter ϵ'' increases with increasing the temperature and hence the most remarkable feature of these parameters are more tendency to their constituent molecules which segregate in space with the creation of interfaces, which is due to the domination of interfacial polarization over dipole polarization. Therefore, it can be concluded that, the interfacial polarization is responsible for the dielectric relaxation of the molecules. During the phase transition from smectic-isotropic region, the molecular twist can be of different liquid crystalline phases, which shows different molecular orientational directions in between these regions. Hence the change in dielectric parameters are remaining same, when it appears nearer to isotropic region, for both parallel and perpendicular orientations and they are giving rise to an overall positive dielectric anisotropy caused by the considerable longitudinal dipole moment. This may lead to the conclusion that the dipole moment exhibits anti-parallel correlations in the isotropic phase of the given molecules (Hourri *et al*., 2002: Hikmet, 1990: Maier *et al*., 1961: Arodz *et al*., 1989: Druon *et al*., 1984: Prasad *et al*., 2006: Humphries *et al*., 1973: Manohar *et al*., 2011: Gupta *et al*., 1979: Arora *et al*., 1978: Johri *et al*., 1971).

Electro-optical studies

An Electro-optical measurement is a very important tool in getting better idea on the phase behavior with electric field at constant temperature. In this experimental study we have considered the sample mixture of 29% BBAA in CN at constant temperature 60 ^{0}C. When the applied voltage increases: the molecular arrangements of liquid crystalline phase start to fluctuate and begin to grow; hence it deforms gradually from the original position. Remarkably it has been observed that, if at constant temperature, the various aspects of low frequency effects on the given mixture show the different directions of molecular re-orientations exhibit flow patterns such as stripped pattern and chevron textures: the formation of zig-zag domains that are characteristic for chevron textures and also the forming time of these patterns depends on the applied voltage. There are significant differences in the electro-mechanical responses of the two textures. The stripe texture does not have a linear electromechanical effect at low fields; only at higher fields the mechanical vibration will have a component of the frequency of the field.

This indicates that the spontaneous polarization has rotated and is no longer parallel to the electric fields. In contrast to the director re-orientations, the layer structure is unchanged by the application of the field. Sequentially we have to increase the applied voltage above 22.05 V, the observed pattern becomes dynamic scattering mode-like and it has been appearing like irregularity of molecular re-orientations of liquid crystalline phase. The new disordered regions arise probably due to the molecules not being confirmed to the orientations in the XZ plane. If the voltage is kept constant for some time, a completely stationary and regular two-dimensional hexagonal grid pattern is observed. The stripped pattern and hexagonal grid pattern textures are as shown in Figure 4 (a, b). The hexagonal grid pattern deforms gradually with increasing frequency and at some stage it becomes indistinguishable from the chevron texture. However: the hexagonal grid pattern is rather stationary and is formed in a short time at 250Hz, 23V. From the Figure 4(a), it follows that: an extremely regular hexagonal grid pattern is formed when the voltage is applied. One of the regions for the formation of hexagonal grid pattern is the electronic charge injected by the applying voltage (Helfrich, 1973: Krishnamurti *et al*., 1979, Kai *et al*., 1975).
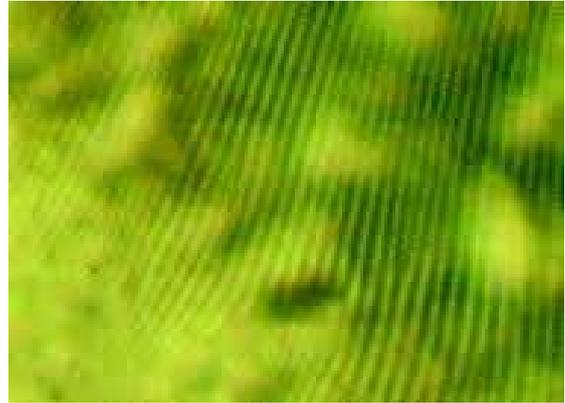
Figure 4(a). Stripped pattern electro-optical texture
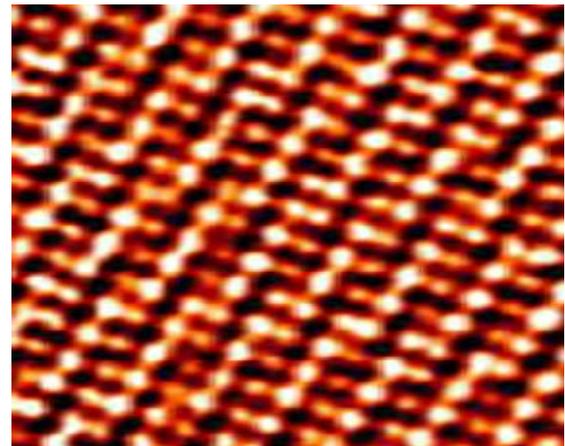
Figure 4(b). Hexagonal grid pattern electro-optical texture

Characterization of nano aggregated grains

The X-ray diffractometer traces obtained for the mixture of 29% BBAA with CN at temperature 49 ^{0}C is shown in Figure 5. The diffraction peaks at this temperature correspond to SmB phase respectively by using JEOL diffractometer with the settings: TC4, CPS400, channel width 100 for λ = 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 (Govindaiah *et al*., 2015:, Theim *et al*., 1979). 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

$L = K\lambda/\beta \cos \theta,$

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, the nano-aggregated grain size of the molecules increases (Kumar, *et al*., 2011: Crosa, *et al*., 1999). Temperature dependent molecular orientations of broken banded focal conic fan texture of smectic-B phase is more stable and hence the molecular ordering of this phase shows two peaks. The nano-aggregated grain size of liquid crystalline material for smectic-B phase comes out to be 42.09 nm. From the X-ray studies, we have observed that, molecular ordering of the liquid crystalline phase increases with decreasing temperature. X-ray studies clearly illustrate that the nano-aggregated grain sizes are big enough to indicate that the molecular ordering (Langford, *et al*., 1978: Lydon, *et al*., 1975: Govindaiah, *et al*., 2015) of layer structure increases as temperature decreases.
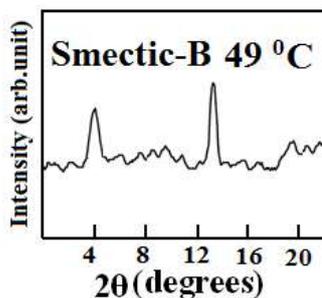
Figure 5. X-ray broadening spectrum for the mixture of 29% BBAA with CN at 49 ^{0}C temperature in SmB phase

Conclusions

In light of the above results, we have drawn the following conclusions. The binary system exhibits a Cho, TGB, SmA, SmC, ReSmA and SmB phases in the different concentrations are at different temperatures. The phase behavior is discussed with the help of phase diagram. A change in the values of dielectric studies shows that the molecules segregate in space with the creation of interfaces, which is due to the domination of interfacial polarization over dipole polarization. This leads to the conclusion that the dipole moment exhibits anti-parallel correlations in the isotropic phase of the given molecules. When applied voltage increases: the molecular arrangements of liquid crystalline phase start to fluctuate and begin to grow; hence it deforms gradually from the original position and it forms hexagonal grid pattern. The X-ray study reveals that the nano-aggregated size of smectic-B phase comes out to be 42.09 nm.

Acknowledgments

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