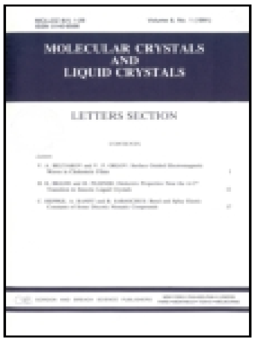

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Phase Diagram Involving the Thermal Stability of TGB and Induced Smectic Phases in Binary Mixture of Thermotropic Liquid Crystals

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ABSTRACT
We report the results of our studies on the optical and thermal properties of the mixture of terephthalidene-bis-4, n-alkylaniline and cholesteryl nonanoate, which exhibits very interesting liquid crystalline mesophases such as cholesteric, twisted grain boundary, smectic-A, smectic-C*, smectic-C, smectic-I, and smectic-G, sequentially when the specimen is cooled from its isotropic phase. These phases have been characterized by using microscopic techniques. The temperature variations of optical anisotropy, electrical conductivity, ultrasonic velocity, and molar and adiabatic compressibility have also been discussed.

KEYWORDS
Adiabatic compressibility; molecular orientation; TGB phase; ultrasonic velocity

Introduction

The twisted grain boundary (TGB) phase of achiral liquid crystal exhibits long-range order that combines a helical twist and smectic layering [1]. This TGB phase, which is an intermediate structure between smectic-A (SmA) and cholesteric phases, is an analog of Abrikosov [2] flux vortex lattice in type-II superconductors, whereas the SmA phase is analogous to the Meissner phase. Indeed, Kamien and Lubbensky [3] have predicted a significant short-range TGB structure in the cholesteric phase at low temperatures, corresponding to a liquid of screw dislocations [4] to be called a chiral line liquid. Therefore, it is recognized as rotated blocks of SmA layers, in which the long molecular axes are arranged normal to the layer planes. Hence, the chiral smectic layers twisted in the molecular axes are expected in the direction of the layer planes [5], and hence the helical axes of TGB phase are perpendicular to the molecular axes and parallel to the smectic planes.

Some of the investigators [6–8] have studied the TGB phase in the mixture of cholesteric and nematic compounds. Lubbensky and Renn [7] have made theoretical predictions in case of TGB-SmA phase transition that it always appears, if the molecular chirality is introduced near the nematic-SmA-smectic-C (SmC) (NAC) multicritical point [8]. In case of TGB-SmA phase, the temperature span Δt should increase with increase in chirality of the system. The TGB-smectic-C* (SmC*) phase has also been close to the NAC point, which is composed of twisted stacks of helical, SmC* phase is also predicted [9].

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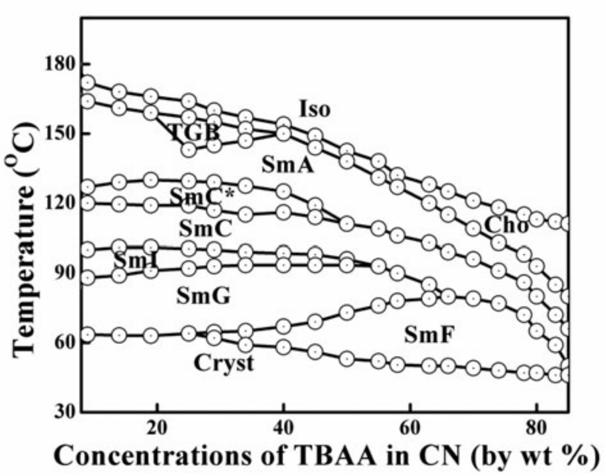


Figure 1. Partial phase diagram for the mixture of TBAA in CN.

In the present investigation, our aim is to carry out the study of optical and thermal properties of the binary mixture of terephthalidene-bis-4, n-alkylaniline (TBAA), and cholesteryl nonanoate (CN) compounds. Some of the concentrations of the mixture exhibit Iso→Cho→TGB→SmA→SmC*→SmC→smectic-I (SmI) →smectic-G (SmG)→Cryst phases sequentially when they are cooled from isotropic phase. They were observed using microscopic technique and also have been verified from the results obtained through optical anisotropic techniques. From the experimentally measured data of ultrasonic velocity, density, and refractive indices, thermodynamic and other related parameters are calculated.

Experimental studies

In the present investigation, we have considered the binary mixture of two thermotropic liquid crystalline materials, viz., TBAA and CN. These materials are obtained from M/s Eastman Organic Chemicals, USA. Mixtures of different concentrations of TBAA in CN were prepared and were mixed thoroughly. Different concentrations of these mixtures 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 density and refractive indices in the optical region are determined at different temperatures by employing the techniques described by the earlier investigators [10–12]. Ultrasonic velocity was measured using a single crystal interferometer working at 2 MHz with an accuracy of $\pm$ 0.05%. Electrical conductivity measurements of the given mixture at different temperatures were carried out using digital LCR meter and a proportional temperature control unit [13].

Results and discussions

Phase diagram

The partial phase diagram shown in Fig. 1, which clearly illustrates that mixtures with concentrations from 9% to 50% of TBAA in CN exhibit a very interesting cholesteric, TGB, SmA, SmC*, SmC, SmI, and SmG phases sequentially when the specimen is cooled from its isotropic melt. But in the concentrations range from 29% to 45% of TBAA in CN shows a cholesteric, TGB, SmA, SmC*, SmC, SmI, SmG, and smectic-F (SmF), respectively, at different temperatures. Above 66%, we have been observed only cholesteric, SmA, and SmF phases. From isotropic region to crystalline region, the phase transition temperature increases, increasing the concentrations of TBAA. The interesting feature of this phase diagram is that it exhibits an unusual sequence of TGB phase with conventional liquid crystalline phases, such as cholesteric, SmA, SmC*, SmC, SmI, and SmG phases are in the mixtures with lower concentrations of TBAA [14]. But in higher concentrations of TBAA, it exhibits only cholesteric, SmA, SmC, and SmF phases, respectively, at different temperatures.

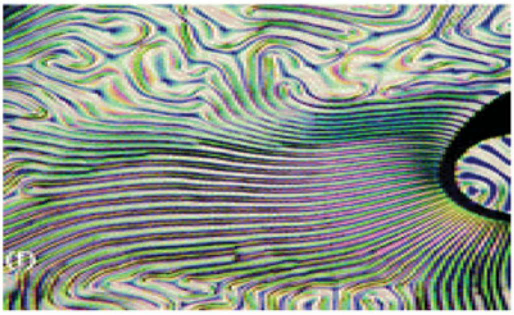
Optical texture studies

A pure CN compound exhibits a planar texture when there is phase transition from isotropic to liquid crystal. The planar texture is characterized by the specular reflection arising from the helicoidal structure of the cholesteric phase. This has a spatial periodicity in the order of the wavelength of light.

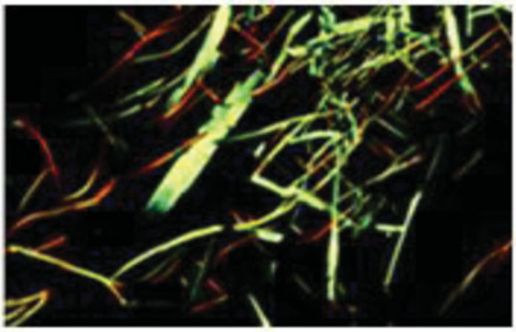
When the molten sample of mixture of 25% of TBAA in CN is cooled from its isotropic phase, nucleation starts in the form of minute bubbles, and immediately, these bubbles grow radially and form a fingerprint pattern, which is characteristic of the cholesteric phase, and the texture so obtained is shown in Fig. 2(a). On further decreasing the temperature, cholesteric phase changes over to the smectic phase, passing through an intermediate phase. The transition to the intermediate phase is assigned by the appearance of mobile streak-like textures in the homeotropic region and they are arranged in a hexagonal form, which is characteristic of TGB phase and the same is shown in Fig. 2(b). On further cooling the specimen, this phase slowly changes over to focal-conic fan-shaped textures, which are the characteristics of SmA phase as shown in Fig. 2(c). The molecular orientation of SmA phase is not energetically stable and then it changes over to SmC* phase, which exhibits a radial fringes on the fans of focal-conic textures, these are the characteristics of chiral SmC* phase. In the same way, orientation of the molecules in SmC* phase is also not stable and then changes over to schlieren texture of SmC phase [15]. Ultimately, the SmC phase undergoes a polymorphic smectic phase transition sequentially in the order SmI, SmG, and SmF phases at lower temperature. Here, the SmI phase is a tilted biaxial phase [16]; the pseudohexagonal molecular packing identifies the molecular structure in the SmI phase, and this phase is hexatic in nature [17]. The molecules in the SmG phase are packed within the layers, having their long axes tilted with respect to normal to the layer planes [18]. In the SmF phase, the molecules are packed in layers, with their long axes tilted with respect to the layer planes [19].

Optical anisotropy

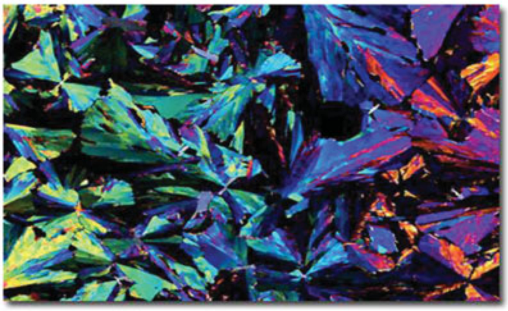
Results of this investigation are further supported by the optical studies. The refractive indices for extraordinary ray (n_e) and ordinary ray (n_o) of the mixture were measured at different temperatures for different concentrations using Abbe refractometer and precession goniometer spectrometer. The temperature variations of refractive indices for 25% of TBAA in CN are as shown in Fig. 3. The value of n_e is greater than n_o, indicating that the material is uniaxial positive. The values of electrical susceptibility for 25% of TBAA in CN have been calculated using Neugebauer relation [20] at different temperatures. The temperature variations of electrical susceptibility for the mixture are as shown in Fig. 4. From the figure, it can be observed that



a) Fingerprint pattern cholesteric phase (250X).



b) Streak like texture of TGB phase (250X).



c) Focal conic fan shaped texture of SmA phase (250X).

Figure 2. Microphotographs obtained in between the crossed polars. (a) Fingerprint pattern cholesteric phase (250X). (b) Streak like texture of TGB phase (250×). (c) Focal-conic fan-shaped texture of SmA phase (250X).

wherever there is an isotropic-liquid crystalline phase transition, the value of electrical susceptibility changes appreciably, which indicates that each change corresponds to the occurrence of different liquid crystalline phases. Further, with increase in the concentration of TBAA, the value of electrical susceptibility decreases with temperature, because the effective optical anisotropy associated with the molecules of TBAA also decreases.

Conductivity measurements

Electrical conductivity measurements help in getting better idea on the phase behavior with temperature. An abrupt increase or decrease of electrical conductivity with temperature

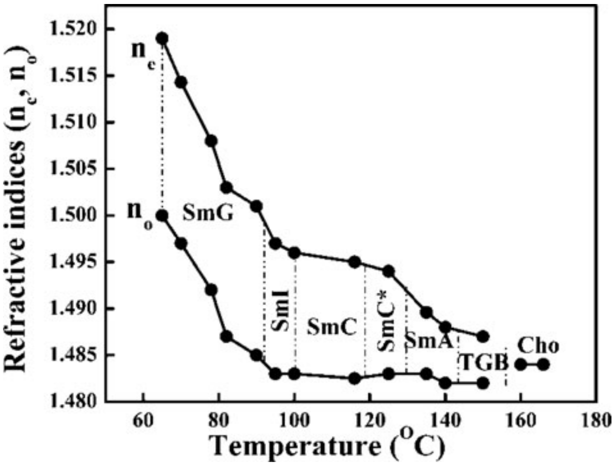


Figure 3. Temperature variations of refractive indices for the mixture of 25% of TBAA in CN.

relates to the phase behavior of the lyotropic and thermotropic systems [21]. The temperature variations of electrical conductivity are shown in Fig. 5, which clearly illustrates that there is some change in the value of electrical conductivity from 70°C to 1160°C, while cooling from isotropic phase for the mixture of 25% of TBAA in CN. In 25% of given mixture, the sequence of phase changes from TGB→SmA→SmC*→SmC→SmI→SmG phases, respectively, at different temperatures. Here, it has been found that the electrical conductivity goes on increasing as the temperature decreases. This suggests that aggregated molecular size starts growing toward lower temperatures and then the system becomes more ordered [22–27].

The temperature variation of ultrasonic velocity adiabatic and molar compressibility

The different mixtures of liquid crystalline materials show an unusual behavior due to their temperature dependent molecular orientation of different properties, which has been attracted considerable attention. An ultrasonic velocity measurement is necessary to getting

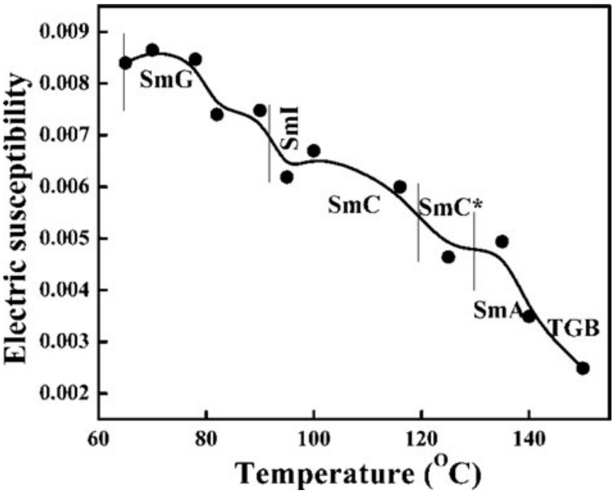


Figure 4. Temperature variation of electrical susceptibility for the mixture of 25% of TBAA in CN.

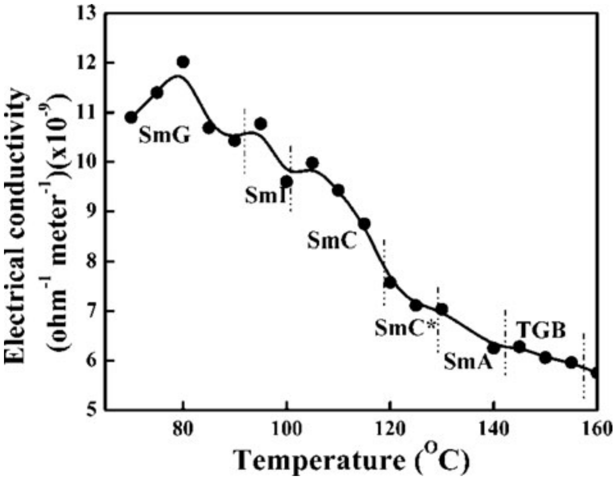


Figure 5. Temperature variation of electrical conductivity σ (Ω^{-1} m^{-1}) for the sample 25% of TBAA in CN.

better idea on the phase behavior with temperature [28]. Molecular orientation of given materials changes with increasing the concentration of one or more addictive substances, and hence the attractive forces are existing between these components. The experimental measurement of ultrasonic velocity shows that attractive forces exist between the mixture of given molecules. Data on some physical properties such as refractive index, ultrasonic velocities, and surface tension are used in extensive applications of chemical engineering process simulation, solution theory, and molecular dynamics [29]. The temperature variation of ultrasonic velocity, adiabatic compressibility, and molar compressibility is presented in Figs. 6(a)–(c). The measured ultrasonic velocity and other related parameters show an anomalous behavior at isotropic-smectic transition. The ultrasonic velocity reaches a minimum value at transition temperature 75°C and increases slightly to a certain extent and then start to decrease by increase in temperature and it shows a different liquid crystalline phase. An increasing ultrasonic velocity has been explained by decreasing the mean distance between the molecules, which clearly shows an increase in potential energy of interaction between the molecules [30,31]. Change in velocity and other related parameters [32] at the transition temperature results from isotropic to smectic phase with long-range orientational order [33]. The adiabatic compressibility [34] increases slightly to a certain value of temperature (75°C) and then start to decrease by increase in temperature and then it increases, increasing the transition temperature toward the isotropic region. The temperature variation of molar compressibility increases linearly with decreasing temperature from isotropic to smectic phase. From this study, the higher value of thermal expansion coefficients is observed in different liquid crystalline phases at different temperatures than in isotropic region, which confirms the tendency of increasing order of molecule with decrease in temperature. Hence, it is firmly established that the ultrasonic velocity and related parameters [35] are structure dependent. Besides depending on the structure, they are related to intermolecular interactions and degree of molecular order in the given mixture. It is well known that the molecules are arranged in order and the orderliness, which increases from cholesteric to smectic phase. The hexagonal, lamellar, and cubic phases are known to exhibit polymorphism at higher and lower temperatures compared to other phases such as cholesteric, nematic, and twisted grain boundary phases [36,37].

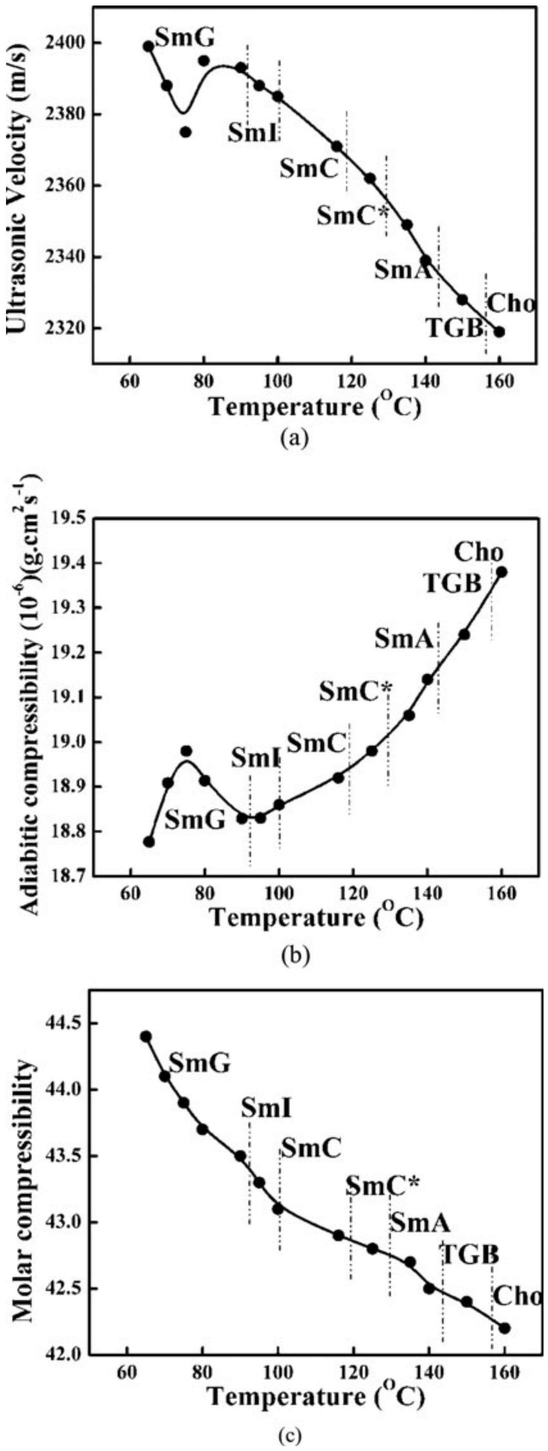


Figure 6. (a) The temperature variation of ultrasonic velocity for the sample of 25% of TBAA in CN. (b) The temperature variation of adiabatic compressibility for the sample of 25% of TBAA in CN. (c) The temperature variation of molar compressibility for the sample of 25% of TBAA in CN.

Conclusions

In light of the above results, we have drawn the following conclusions. The binary system of two compounds exhibits an unusual sequence of phases, showing the formation of TGB and induced smectic phases, respectively, at different concentrations at different temperatures. The phase behavior is discussed with the help of phase diagram. The changes in value of electrical conductivity with the variation of temperature unambiguously correspond to smectic-cholesteric phase transition. Drastic changes in the values of electrical conductivity are expected to be due to changes in the dimension of discs along with changes in the orientation order of the arrangement. The anomalous behavior of liquid crystalline physical properties such as ultrasonic velocity, adiabatic compressibility, and molar compressibility are discussed at the isotropic mesophase transition.

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