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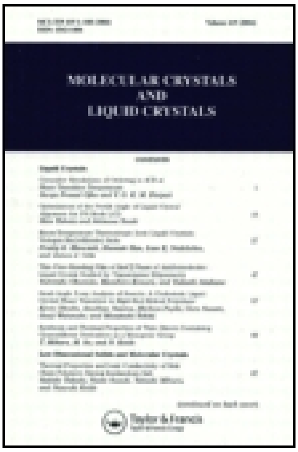

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Optical and Thermal Characterization of Binary Mixtures of Liquid Crystals

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Optical and Thermal Characterization of Binary Mixtures of Liquid Crystals

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We report the results of our studies on the optical and thermal properties of the mixture of cholesteryl nanonate, cetyl-dimethyl-ethylammonium bromide, and ethylene glycol, which exhibits very interesting liquid crystalline mesophases like cholesteric (N) and induced smectic phases, such as SmA, SmC*, SmE, and SmB, sequentially when the specimen is cooled from its isotropic liquid phase. These phases have been characterized by using differential scanning calorimetric, X-ray diffraction, and optical texture studies. The pitch of the cholesteric phase is discussed. The temperature variation of optical anisotropy, electrical conductivity, ultrasonic velocity, molar, and adiabatic compressibility has also been discussed.*

Keywords Binary mixture; molecular orientation; optical texture and optical anisotropy; phase diagram; ultrasonic velocity

Introduction

A crystal is highly ordered and solid. A liquid is fluid, isotropic, and has no order. Liquid crystal materials are fluid but viscous and have turbid appearance. As in the crystalline state, an orientational order of the molecules, due to short-range interactions between the molecules, the lack of positional ordering in three dimensions gives its fluid character [1–3]. The fluidity of liquid crystal depends onthe organization within liquid crystalline phases such as nematic, smectic, and cholesteric phase. Nematic phases have low viscosities, but all smectic and most cholesteric phases are highly viscous. In many of the cases, it is necessary to move the cover slip ascertain the fluid of sample: the texture of liquid is deformed upon shearing, whereas crystalline film breaks [4].

Thermodynamic and transport properties of the liquid crystalline materials provide useful information about physical forces acting between the molecules of the pure compounds and additive substances. The mixture of mesomorphic and nonmesomorphic materials is get-together, the structure of layer undergoes a change in conformation in response to the molecular interaction, the results of changes in physical and thermodynamic properties can be considered as a sum of several contributions due to free volume change, change in energy, change in molecular orientations, steric hindrances, etc. As the orientational order

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*Address correspondence to T. N. Govindaiah, Post-Graduate Department of Physics, Government College (Autonomous), Mandya 571401, Karnataka, India. E-mail: pgphysicsfaculty@gcm.ac.in of the molecules in mesomorphic compound changes with increasing the concentration of additive substances and hence, the attractive force between the component molecules, a measure of ultrasonic velocity, compressibility, viscosity, and absorption should give the nature of attractive forces existing between the two types of molecules [5–8].

In the present investigation, our aim is to study the mixture of mesogenic and nonmesogenic compounds, namely, cholesteryl nanonate (CN), cetyl-dimethyl-ethylammonium bromide (CDEAB), and ethylene glycol (EG), which exhibits a very interesting liquid crystalline cholesteric phase and induced smectic phases, such as SmA, SmC*, SmE, and SmB phases, respectively, at different temperatures. They were observed using microscopic technique and also have been verified from the results of differential scanning calorimetric (DSC), X-ray, and optical anisotropic techniques. From the experimentally measured data of ultrasonic velocity, density, and refractive indices, thermodynamic and other related parameters are calculated. Helfrich potential and elastic moduli have been estimated in the various liquid crystalline phases, using Helfrich model with approximation.

Experimental Studies

In the present study, we use the materials, namely, CN, CDEAB, and EG. Mixtures of 25 different concentrations of CN in CDEAB + EG 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 coverslip and were sealed for microscopic observations. DSC thermograms were taken for mixtures of all concentrations, using the Perkin-Elmer DSC II Instrument facility available at Raman Research Institute, Bangalore, India. The DSC thermogram for the sample of 33% CN in CDEAB + EG is shown in Fig. 1. The sequence of occurrence of different phases is as follows:

I – 113°C, Ch – 97.4°C, SmA – 77°C, SmC* – 60°C, SmE – 52.8°C, SmB – 43.5°C

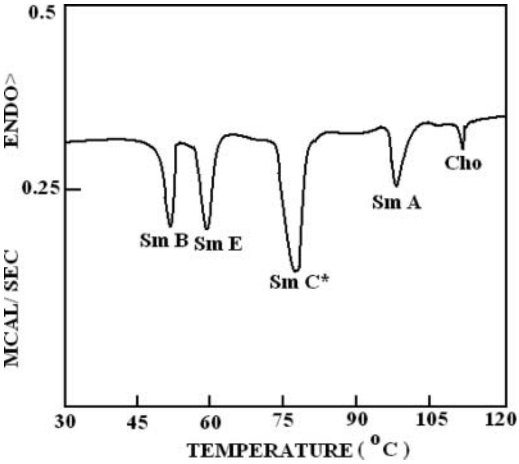

Figure 1. DSC thermogram for the samples of 33% of CN in CDEAB + EG.

The X-ray diffraction studies were undertaken by using Jeol X-ray diffractometer at various temperatures for different concentrations. Ultrasonic velocity was measured using a single crystal interferometer working at 2 MHz with an accuracy of ±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.

Results and Discussion

Phase Diagram

Mixture of CN in CDEAB and EG exhibits very interesting different liquid crystalline phases, and the phase transition temperatures are measured by using Leitz-polarizing microscopic. The partial phase diagram is shown in Fig. 2, and it is obtained by plotting the concentrations against the phase transition temperatures of the mixture, which clearly illustrates that the mixture of all concentrations of CN in CDEAB + EG exhibits a cholesteric phase and also an induced smectic phases, such as SmA, SmC*, SmE, and SmB phases, respectively, at different temperatures, when the specimen is cooled from its isotropic liquid phase. The concentrations of the mixture from 10% to 55% of CN show an unusual chiral SmC* phase, but in the range from 38% to 42% of CN, SmC* phase decreases and hence increases from 42% to 55% of CN. The range from 5% to 48% of CN shows SmE phase and from 5% to 60% of CN shows SmB phase, which remains up to room temperature.

Optical Texture Studies

For the purpose of optical texture studies, the sample was sandwiched between the slide and cover glass, and then the optical textures were observed using Leitz-polarizing microscope in conjunction with specially constructed hot stage. The concentrations of the mixture ranges from 5% to 60% are slowly cooled from its isotropic melt, the genesis of nucleation starts in the form of small bubbles and these bubbles slowly grow radially and form a

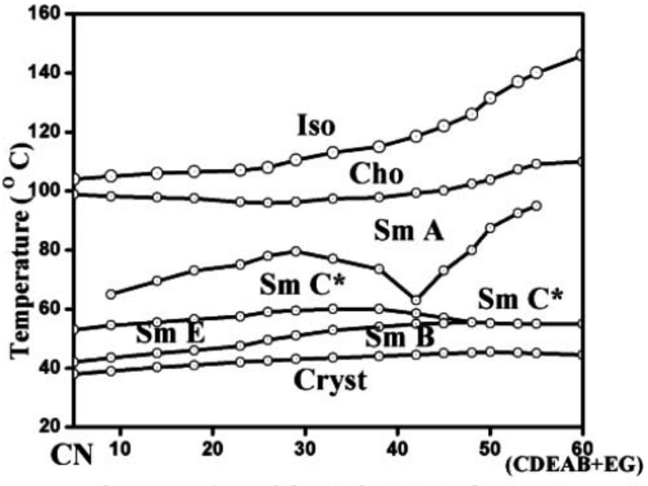

Figure 2. Partial phase diagram for the mixtures of CN in CDEAB + EG.

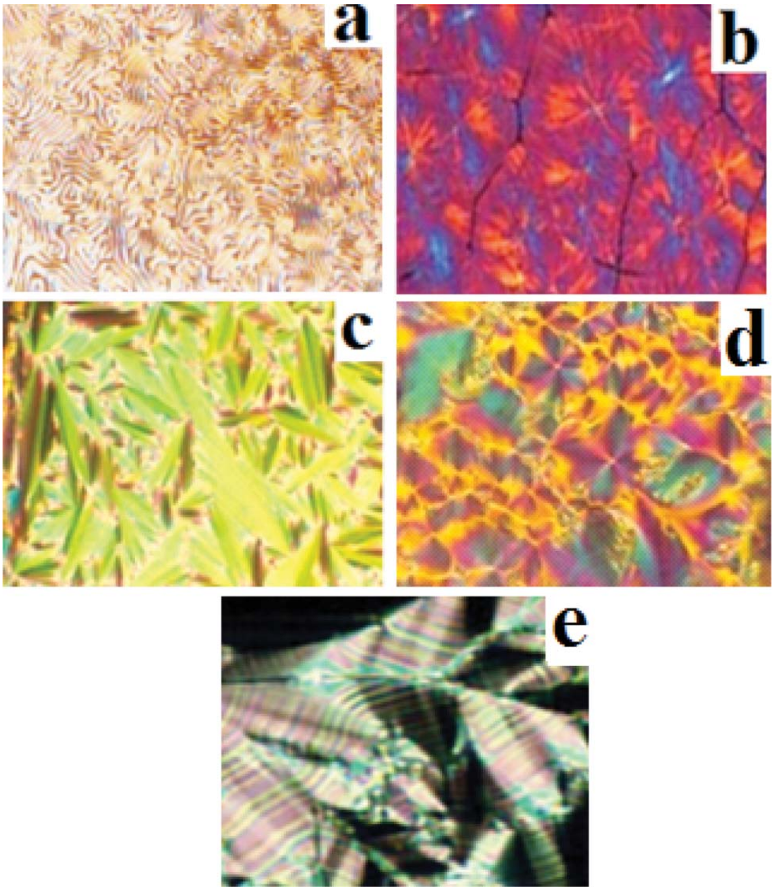

Figure 3. Microphotographs showing (a) fingerprint pattern cholesteric phase (185×), (b) spherulite texture of cholesteric phase (185×), (c) focal-conic fan-shaped texture of SmA phase (180×), (d) schlieren texture of chiral SmC* phase (180×), and (e) Fan-shaped texture of SmE phase (180×) (color figure available online).

fingerprint pattern, which is the characteristic of cholesteric (N*) phase with large values of pitch as shown in Fig. 3(a) [9,10]. However, the mixtures with higher concentrations of CN in CDEAB + EG that exhibit beautiful spherulitic textures of cholesteric phase were observed with low viscous molecular orientation. Spherulitic texture of cholesteric (N*) phase is shown in Fig. 3(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. 3(c). The concentrations of the mixture ranges from 10% to 55%, the SmA phase 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 as shown in Fig. 3(d). On further cooling the specimen, the Smc* phase changes over to SmE phase as shown in Fig. 3(e), and then it changes over to SmB phase, which remains up to room temperature, and then it becomes a crystalline phase.

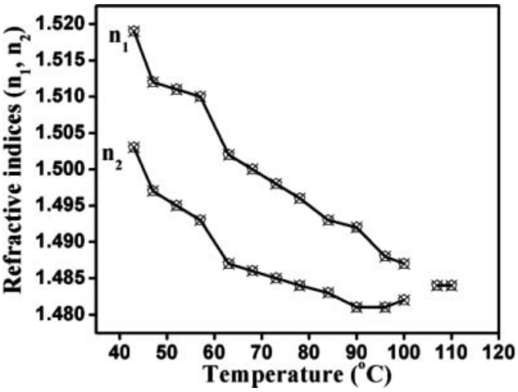

Figure 4. Temperature variation of refractive indices for the mixture of 29% CN in CDEAB + EG.

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 29% of CN in CDEAB + EG are shown in Fig. 4. The value of n_e is greater than that of n_o, indicating that the material is uniaxial positive. The values of electrical susceptibility for 29% of CN in CDEAB + EG have been calculated using Neugebauer relation [11] at different temperatures. The temperature variations of electrical susceptibility for the mixture are shown in Fig. 5. From the figure, it can be observed that 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. Furthermore, with increase in the concentration of CN, the value of electrical susceptibility decreases with temperature, because the effective optical anisotropy associated with the molecules of CN also decreases.

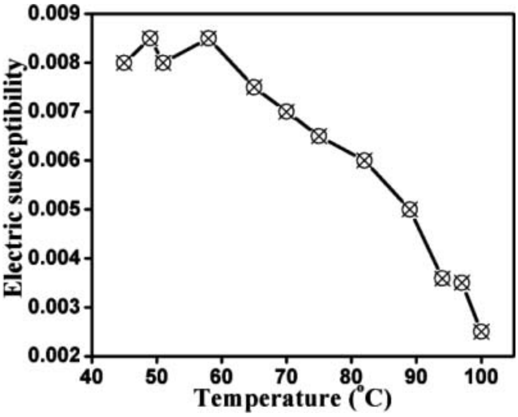

Figure 5. Temperature variation of electric susceptibility for the mixture of 29% CN in CDEAB + EG.

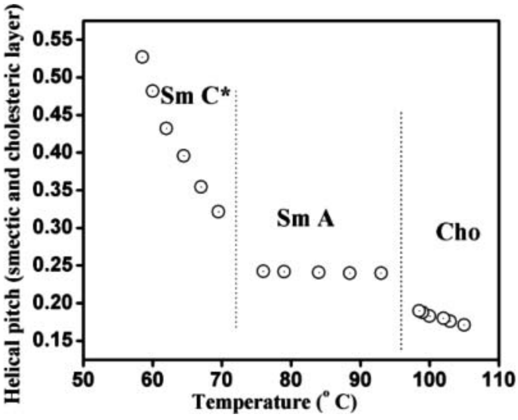

Figure 6. The temperature variations of pitch for the mixture of 18% CN in CDEAB + EG.

Helical Pitch Measurements

The helical pitch measurements were performed on the cholesteric phase after the well-known Grandjean–Cano wedge method [12,13]. The mixture was taken in a wedge-shaped cell treated for homogeneous alignment. The two glass plates formed a small angle at the wedge. The mixture was cooled slowly (0.2°C min^{-1}) from the isotropic phase to the smectic phase, which induced an array of equidistant Grandjean–Cano lines. The pitch of the cholesteric phase was determined by measuring the distance between the Grandjean-Cano lines as a function of temperature. As the temperature was lowered from the cholesteric phase to smectic phase, the spacing between the lines increased, indicating that the pitch in this phase was increasing. The temperature variation of pitch for the mixture of 18% CN in CDEAB + EG is shown in Fig. 6. From this figure, it is evident that the variation of pitch from the cholesteric phase to smectic phase is smooth and continuous. But the value of pitch gradually increases from 0.17 mm to 0.19 mm was observed upon cooling the sample from cholesteric phase to smectic phase. The value of the pitch increased steeply and reached a maximum of 0.55 mm at the cholesteric to smectic phase transition. But, in the study, we have been notice that the sequence is Iso-Cho-SmA-SmC*-SmE-SmB on heating. Most of the data about the helical pitch have been previously given in reference [14]. The pitch is continuous at the cholesteric to SmA transition in spite of a rather energetic transition. It increases on cooling to smectic phase and diverges on approaching the SmA and SmC* phases. This divergence related to the second order nature of the transition. It exhibits a steep decrease, close to cholesteric phase, which is usually characteristic of second-order SmA, SmC* transitons.

X-Ray Studies

To understand the change in layer spacings in SmA and SmC* phases with respect to temperature, X-ray diffractometer traces were taken. The traces obtained for the mixture of 33% CN in CDEAB + EG at different temperature correspond to SmA and SmC* phases. It is observed that as the temperature increases, the layer spacing also increases in SmC*phase, but in SmA phase, the layer spacings are almost constant, and these variations are shown in Fig. 7 [15–17].

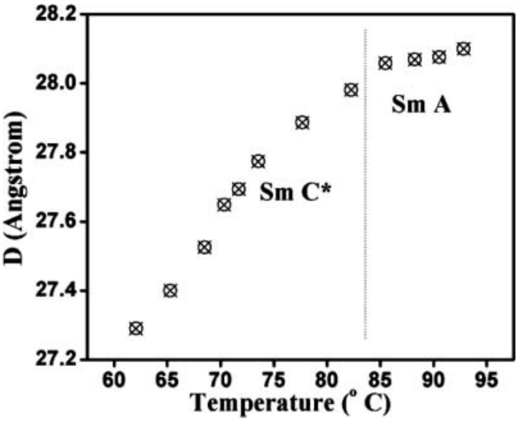

Figure 7. Variation of layer spacing with temperature for the sample of 33% of CN in CDEAB + EG.

Conductivity Measurements

To obtain reliable data on the phase behavior with temperature, electrical conductivity measurements are necessary. An abrupt increase or decrease of electrical conductivity with temperature relates to the phase behavior of the lyotropic and thermotropic systems [18]. The temperature variations of electrical conductivity are shown in Fig. 8. The changes were observed in electrical conductivity, the values correspond to liquid crystalline phase transition of thermotropic and lyotropic systems, respectively, at different temperatures, and they were also identified by DSC and optical texture studies. It was observed that a change in electrical conductivity at temperatures 47.5°C, 57.5°C, 72°C, 96°C, and 108°C, respectively, corresponds to phase transition from SmB to SmE, SmE to SmC*, SmC* to SmA phase, and SmA to cholesteric phase. This type of behavior is generally observed in hexagonal, cubic, and lamellar phase of lyotropic and thermotropic systems [19,20].

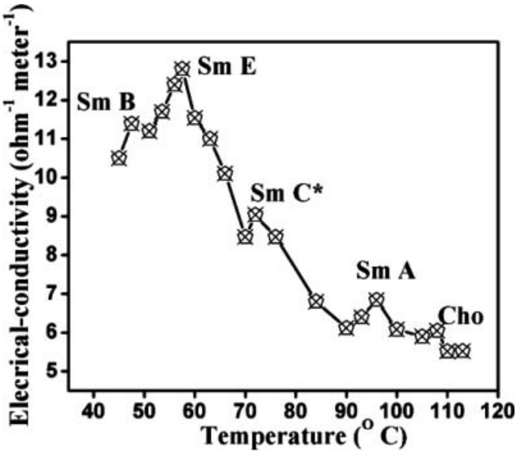

Figure 8. Temperature variation of electrical conductivity σ (Ω^{-1} m^{-1}) for the sample of 33% of CN in CDEAB + EG.

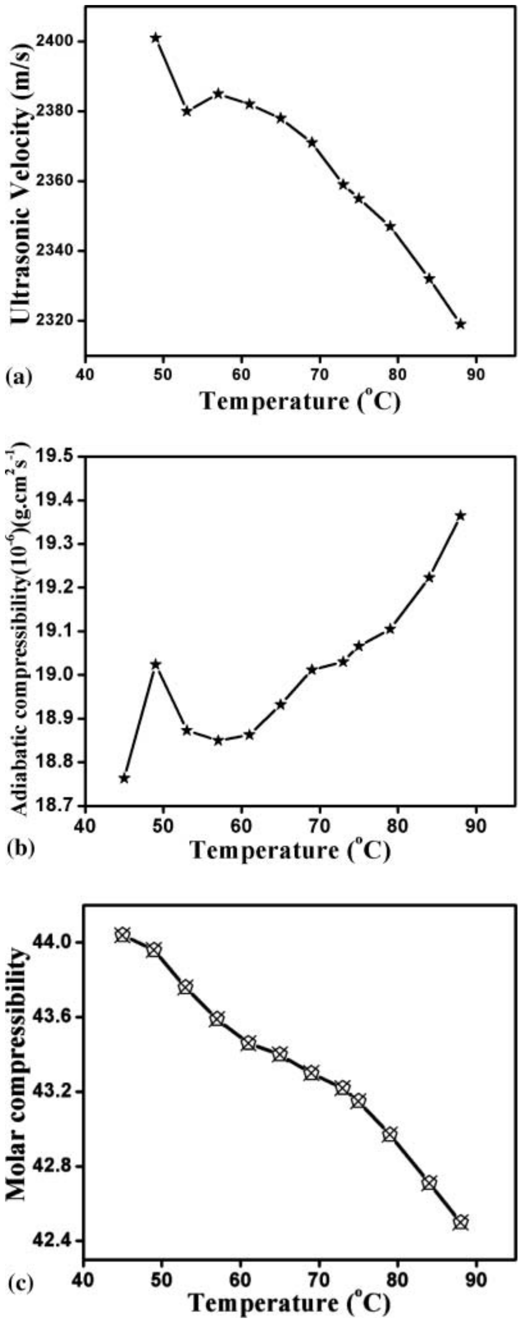

Figure 9. (a) The temperature variation of ultrasonic velocity for the sample of 33% of CN in CDEAB + EG. (b) The temperature variation of adiabatic compressibility for the sample of 33% of CN in CDEAB + EG. (c) The temperature variation of molar compressibility for the sample of 33% of CN in CDEAB + EG.

The Temperature Variations of Ultrasonic Velocity, Adiabatic, and Molar Compressibility

The mixtures of liquid crystalline materials due to their unusual behaviors have very attracted considerable attention. To obtain reliable data on the phase behavior with temperature, ultrasonic velocity measurements are necessary [21]. As the orientational order of the molecules in mesomorphic compound changes with increasing the concentration of one more addictive substance and hence, the attractive force between the components of the molecules, the measure of ultrasonic velocity, absorption should give the nature of attractive forces existing between the mixtures of the given molecules. Data on some of the properties associated with the like refractive index, ultrasonic velocities, and surface tension find extensive application in chemical engineering process simulation, solution theory, and molecular dynamics [22]. The temperature variation of ultrasonic velocity, adiabatic compressibility, and molar compressibility is shown in Fig. 9(a)–(c). The velocity exhibits an anomalous behavior at the isotropic mesophase transition while it varies linearly in the isotropic and mesomorphic phase away from transition. The velocity shows a dip at the transition. The ultrasonic velocity and related parameter show anomalous behavior of isotropic mesophase transition of the liquid crystals. The ultrasonic velocity linearly increases in isotropic phases up to the transition with decreasing temperature [23,24]. The increase in velocity is explained as the decrease in mean distance between the molecules, thereby increasing the potential energy of the interaction between the molecules. The velocity reaches a minimum at the transition temperature and increases sharply below the transition, and then it shows a linear increase in mesophase. The change in velocity and other parameters [25] at the transition results from disordered molecular arrangement in isotropic phase to an ordered arrangement of molecules in the liquid crystalline phase with long-range orientational order [26]. The variation of adiabatic compressibility [27] is remarkably linear in the isotropic and mesomorphic phases, but it shows a step jump at the isotropic-mesomorphase transition. The result of molar compressibility varies linearly with temperature at the isotropic phase transition. In this study, the higher values of thermal expansion coefficient in mesophase than in the isotropic phase confirm the tendency of increasing order of molecule with decrease in temperature. Hence, it is firmly established that the ultrasonic velocity and related parameters [28] are structure dependent. Besides, depending on the structure, they are related to intermolecular interactions and degree of molecular order in liquid crystalline mixture. It is well known that in liquid crystalline phases, the molecules are arranged in order and the orderliness increases from cholesteric to smectic phase. The hexagonal, lamellar, and cubic phases are known to exhibit polymorphism at higher and lower temperature compare to other phases such as cholesteric, nematic, and twisted grain boundary phases [29,30].

Conclusions

In light of the above results, we have drawn the following conclusions. The multicomponent system of mesogenic and nonmesogenic compounds exhibits an unusual sequence of phases, showing the formation of induced chiral smectic phases in the concentration range of 10% to 55% of CN in (CDEAB + EG). 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 and cholesteric phases. Drastic changes in electrical conductivity are expected to be due to changes in the dimension of disks along with changes in the orientation order of the arrangement. X-ray and DSC studies also lend support to these observations. The anomalous behavior of liquid crystalline physical properties, such as ultrasonic velocity, adiabatic compressibility, and molar compressibility, is discussed at the isotropic mesosphere transition.

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