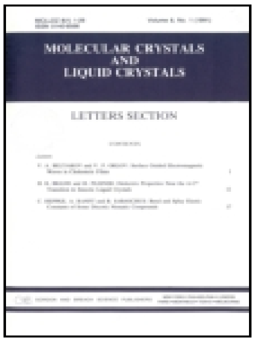

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Studies on Anisotropic Molecular Orientation and Mesophase Stability in a Ternary Mixture of Liquid Crystalline Materials

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ABSTRACT
The multicomponent system of cholesteryl linolenate (CL), sodium oleate (Naol), and orthophosphoric acid (H_3PO_4) exhibits liquid crystalline mesophases, like cholesteric and smectic phases, such as SmA, SmC, SmB, and SmG sequentially when the specimen is cooled from its isotropic phase. These phases have been observed by using microscopic technique. Helfrich potential and elastic moduli have also been estimated in the smectic phase using Helfrich model. Optical transmittance and electrical conductivity have also been discussed.

KEYWORDS
Helfrich potential; molecular orientation; optical anisotropy; optical transmittance; phase stability

Introduction

Liquid crystals are partly ordered materials, somewhere between their solid and liquid phases. This means that liquid crystal combines fluidity of ordinary liquids with the interesting electrical and optical properties of crystalline solids. Liquid crystals are temperature sensitive, since they turn into solid if it is too cold and into liquid if it is too hot. This phenomenon can, for instance, be observed on laptop screens when it is very hot or very cold. Molecules in a liquid crystal are often shaped like rods or plates or some other forms that encourage them to that align collectively along a certain direction. An external perturbation, such as change in temperature or magnetic field, even very small can induce the liquid crystals to assume a different phase. The molecules in liquid crystal display for instance are reoriented by relatively by weak electrical fields. Different phases can be distinguished by their different optical properties [1, 2].

Liquid crystal phases that respond to certain temperature ranges are called the thermotropic phases. Many thermotropic liquid crystals exhibit a variety of phases as temperature is changed. The ordering inside a thermotropic liquid crystals exists in a specific temperature range. At high temperature, the thermal motion will destroy the delicate cooperative ordering of the liquid crystal phase, pushing the material into a conventional isotropic liquid phase. At too low a temperature, most liquid crystal materials will form a conventional crystal. The intermediate phases will have some level of order, which is progressively lost as the temperature rises. In the smectic phases, which are found at lower temperature than the nematic, molecules form well defined layers that can slide over one another. The smectics have positional order in one direction. In the nematic phase, the molecules have no positional order but

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they have long-range orientational order. This means that the molecules move quiet randomly but they all point in the same direction (within each domain) [3, 4].

In the present investigation, our aim is to study the mixture of multicomponents, namely, cholesteryl linolenate (CL), sodium oleate (Naol), and Orthophosphoric acid (H_3PO_4), which exhibits liquid crystalline cholesteric phase and smectic phases, such as SmA, SmC, SmB, and SmG phases, respectively, at different temperatures. They were observed using microscopic technique and also been verified from the results of optical anisotropic techniques. Helfrich potential and elastic moduli have been estimated in the smectic phases using Helfrich model with approximation.

Experimental section

The compound sodium oleate (Naol) 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. Orthophosphoric acid (H_3PO_4) was supplied from Kodak, Ltd., Kodak house, Mumbai, India. Cholesteryl Linolenate was obtained from M/s Eastman Organic Chemicals USA. Mixtures of 20 different concentrations of CL in (Naol + H_3PO_4) 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.

Polarizing microscopic studies

Polarizing microscopic technique is the most widely used method in identifying different phases. Liquid crystalline substance is placed between two glass cover slips. Depending on the boundary condition and the type of phase, various textures which are characteristics of a phase are observed. Usually the texture changes while going from one phase to another. Polarizing microscopy is a powerful tool when used in combination with miscibility of binary mixtures. Liquid crystalline phases possess characteristic textures when viewed under polarized light. These textures, which can often be used to identify phases, result from defects in the liquid crystals. Polarizing Microscopy is used for identifying the various phases like Nematic, Cho, TGB and induced smectic phases such as SmA, SmB, SmC*, SmC, SmE, etc. As the liquid crystalline material goes from solid to liquid crystalline phase, the degree of order decreases. This is expressed by decrease in the value of order parameter. In case of orientational disorder it is possible to see changes between different liquid crystal phases during the heating and cooling cycles of liquid crystals.

Refractive index measurement

Refractive index has been measured using Abbe's Refractometer. A polarizer has been introduced in Abbe's refractometer to block the extraordinary ray, which clears the contrast of the boundary line at view of Refractometer. To calculate birefringence Δn following relation has been used $\Delta n = n_e - n_o$ The temperature of Abbe's Refractometer is controlled by circulating heated oil using JULABO F-25, refrigerated circulator. The temperature was measured by placing a thermocouple in close vicinity of the sample with an accuracy of $+0.1°C$.

Optical transmittance measurement

For the Optical Transmittance Measurement, the sample was in to the standard sample holder pretreated for planar alignment having 5 μm spacer by heating it 10°C above the clearing point of the sample and then introducing the sample at one end of the holder it was filled in the sample holder by the capillary action and sample holder was slowly cooled up to the room temperature. Now sample holder is placed between two crossed polarizer of polarizing microscope model CENSICO (7626) fitted with a hot stage and light intensity coming through the eyepiece has been measured by light-dependent resistance (LDR). The resistance value of LDR corresponding to varying light intensity due to temperature variation of the sample is proportional to the inverse of optical transmittance and has been directly measured by attached digital multimeter.

Electrical conductivity measurements

The electrical conductivity measurements were carried out at different temperatures in the heating/cooling cycles, with the constant rate of scanning 2°C/min. The temperature was stabilized using a homemade thermoelectric cooler, based on Peltje elements and it was recorded by a Teflon-coated K-type thermocouple (±0.1°C) and it was connected to the data logger thermometer center 309 (JDC Electronic SA, Switzerland). The unoriented samples were used and the conductometric cell included two horizontal platinum electrodes of 14 mm in diameter, with 0.5 mm interelectrode space. Before the measurements, the cell parts were washed in hexane and dried at 117°C. The electrical conductivity of the samples was measured by the inductance, capacitance, and resistance (LCR) meter 819 (Instek, 12 Hz–100 kHz). The measurements were done under the applied external voltage of 1 V and frequency of 500 Hz. This frequency was selected for avoidance of significant polarization effects on the electrodes.

Results and discussions

Phase diagram

The ternary mixtures of CL in (Naol + H_3PO_4) exhibit various liquid crystalline phases. The phase transition temperatures were measured by using Leitz-polarizing microscope. The partial phase diagram shown in Fig. 1, which is obtained by plotting the concentrations against the phase transition temperatures of the mixture, clearly illustrates that, the concentrations ranging from 5% to 50% concentrations of CL in (Naol + H_3PO_4) exhibit cholesteric phase and also induced smectic phases like SmA, SmC, SmB, and SmG phases, sequentially when the specimen is cooled from its isotropic liquid phase [5]. The phase behavior is discussed with the help of phase diagram (Fig. 1).

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 hot stage. The concentrations ranging from 5% to 50% of the given mixture are slowly cooled from its isotropic melt. The genesis of nucleation starts in the form of small bubbles and slowly grow radially, which form a spherulitic texture of cholesteric phase with large values of pitch and texture is as shown in Fig. 2(a) [6, 7] at temperature 110°C. On further

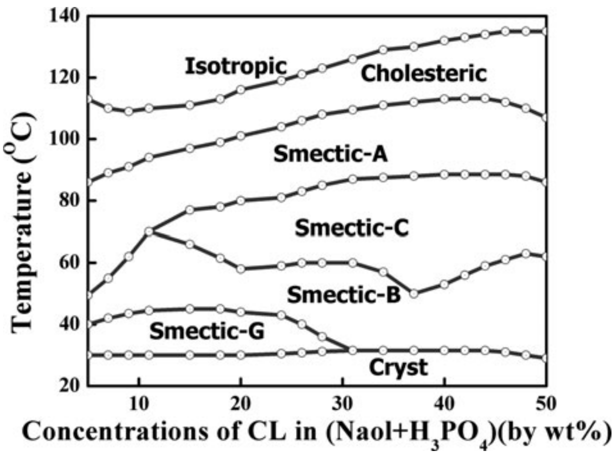
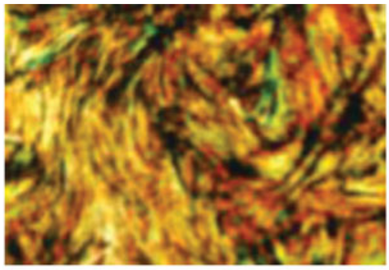


Figure 1. Partial phase diagram for the mixture of CL in (Naol + H_3PO_4).

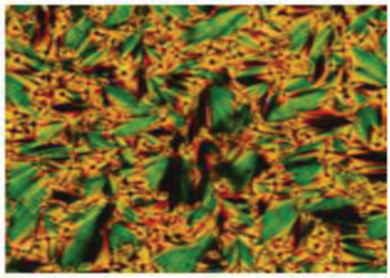
cooling the specimen, the cholesteric phase slowly changes over to focal conic fan shaped texture, which is the characteristics of SmA phase and is as shown in Fig. 2(b) at temperature 92°C. On further cooling the specimen, SmA phase changes over to schlieren texture of SmC phase, which is as shown in Fig. 2(c) at temperature 70°C and then it changes over to SmB phase. Before crystallization of the specimen, SmB phase changes over to a broken banded focal conic fan texture of chiral SmG phase, as shown in Fig. 2(d) at temperature 35°C. If the constituent molecules of the materials, which exhibits a SmG phase is of chiral nature, then the phase itself may also be weakly optically active; it is then termed as chiral SmG phase [8]. 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, each of tilts are within the same direction. However, in the layer above and below, the tilt direction will 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 [9] and the same texture is retained up to room temperature.

Refractive indices

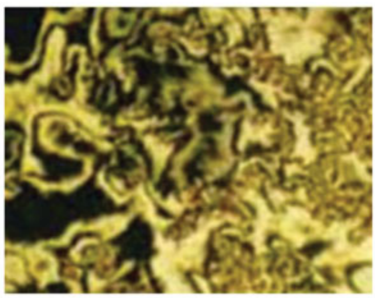
Results of this investigation are further supported by the optical studies. The refractive indices for extraordinary ray (n_e) and ordinary ray (n_o) of the mixture were measured at different temperatures for the different concentrations using Abbe Refractometer and Precision Goniometer Spectrometer. The variations of refractive indices as a function of temperature for 24% of CL in (Naol + H_3PO_4) are 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 24% of CL in (Naol + H_3PO_4) have been calculated using Neugebauer relation [10] at different temperatures. The variation of electrical susceptibility as a function of temperature for the mixture is shown in Fig. 4. From the figure, it can be observed that wherever there is phase transition, the value of electrical susceptibility changes appreciably, which indicates that the changes correspond to various smectic modifications. Further, with increase in the concentration of CL, the value of electrical susceptibility decreases with temperature, because the effective optical anisotropy associated with the molecules of CL also decreases.



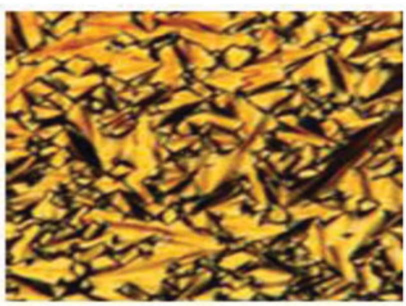
a) Spherulitic texture of cholesteric phase at temperature 110 ^{0}C (250X).



b) Focal conic fan shaped texture of SmA phase at temperature 92 ^{0}C (250X).



c) Schlieren texture of SmC phase at temperature 70 ^{0}C (250X).



d) Broken banded focal conic fan texture of chiral SmG phase at temperature 35 ^{0}C (250X).

Figure 2. Microphotographs obtained in between the crossed polars, (a) Spherulitic texture of cholesteric phase at temperature 110°C (250×). (b) Focal conic fan shaped texture of SmA phase at temperature 92°C (250×). (c) Schlieren texture of SmC phase at temperature 70°C (250×). (d) Broken banded focal conic fan texture of chiral SmG phase at temperature 35°C (250×).

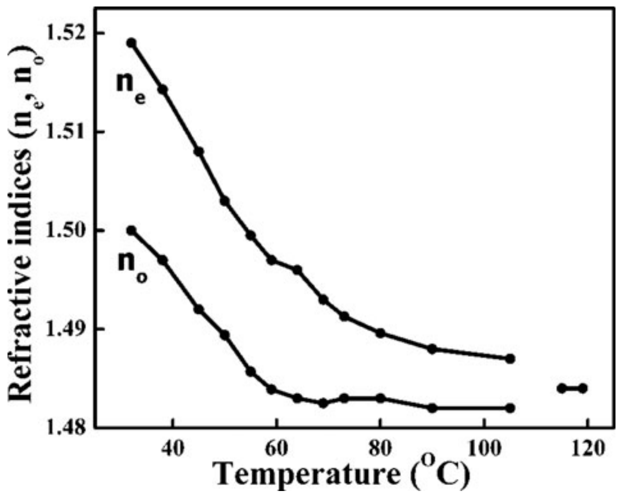


Figure 3. Temperature variations of refractive indices for the mixture of 24 % CL in (Naol + H_3PO_4).

Helfrich potential and elastic modulus

The free energy of steric intermembrane interactions exists between undulating neighboring membranes, when they are side by side in the multilayer systems [11]. The undulation modes in multilayer systems can be treated in terms of the de Gennes theory [12] of fluctuations in smectic phase, which invokes curvature elasticity and smectic compressibility. To estimate the Helfrich potential [$V(\xi)$], we consider the free energy per unit area

$$V(\xi) = \beta \frac{(k_B T)^2}{k_0 \xi^2} \tag{1}$$

where $\beta = 3p^2/128$, $(k_0/k_B\ T) = 0.75$ (The repulsive force between the membrane), k_0 = bare bending constant, k_B is the Boltzman constant. The $V(\xi)$ of membrane varies with inverse square of the membrane spacing assuming that the local tilt of the membrane induced by undulations remains in effect well below $\pi/2$. ξ is the mean membrane separation. Here, it has been considered that the value of "ξ" is equal to the value of d [12].

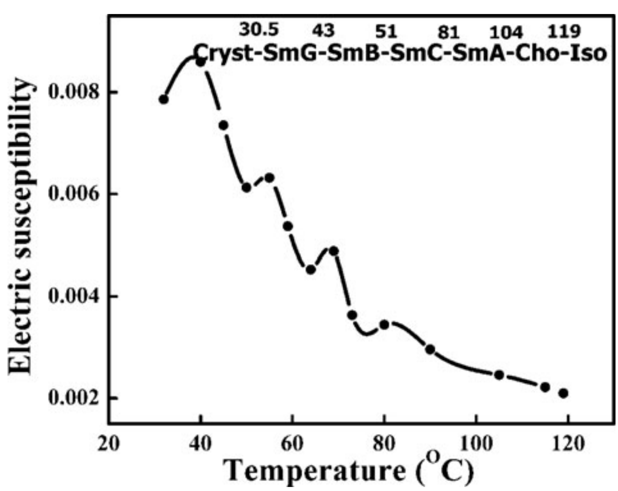


Figure 4. Temperature variation of electrical susceptibility for the mixture of 24 % CL in (Naol +H_3PO_4).

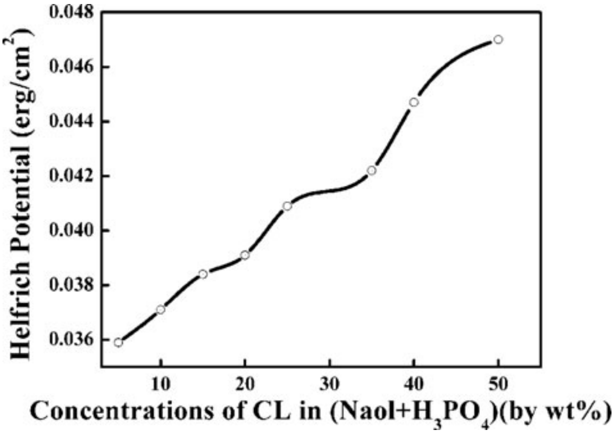


Figure 5. Variation of Helfrich potential with concentrations of CL in (Naol + H_3PO_4).

The variation of Helfrich potential with the concentrations of CL in (Naol + H_3PO_4) is shown in Fig. 5. From the graph, it is observed that, Helfrich potential increases as the concentration CL in the mixture increases. This result invokes that in dilute region of the mixture $V(\xi)$ value decreases.

The elastic modulus (K) [12] of smectic compressibility is calculated using the relation

$$K = \frac{3\pi^2}{64}\frac{(k_B T)^2}{k_c d} \tag{2}$$

where k_c is curvature elastic modulus.

The elastic modulus is also estimated for the mixture of different concentrations at various temperatures [13]. The graph obtained by plotting the elastic modulus as a function of the concentrations of CL in (Naol + H_3PO_4) is presented in Fig. 6. From the graph it is observed that, as the concentration of CL decreases, value of the bulk modulus also decreases. The small values of electrical susceptibility, bulk modulus, and Helfrich potential in low concentrations are due to the lesser value of density in which the interaction of smectic layers with the neighboring layers appears to be very less.

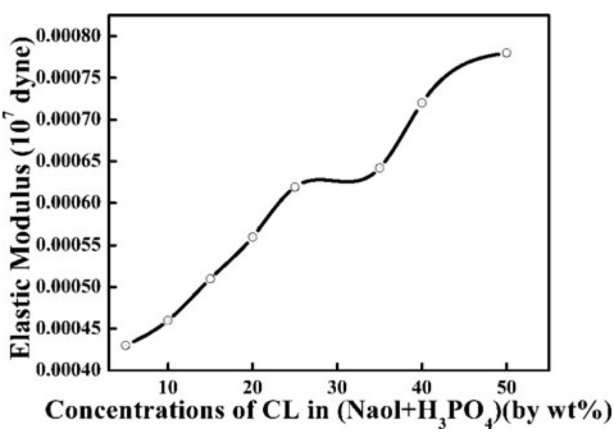


Figure 6. Variation of Elastic modulus with concentrations of CL in (Naol + H_3PO_4).

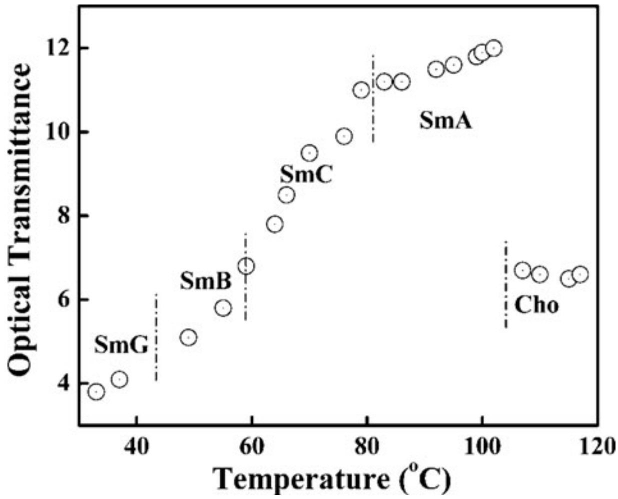


Figure 7. The temperature variations of optical transmittance for the mixture of CL in (Naol + H_3PO_4).

Optical transmittance studies

The temperature variation of optical transmittance for the mixture of 24% of CL in (Naol + H_3PO_4) is shown in Fig. 7. Which clearly illustrates that, the value of optical transmittance increases slowly with increase temperature from 33°C to 102°C, while the sequence of phase appear from crystalline region to near isotropic region and suddenly there is some changes observed in the value of optical transmittance from 107°C to 117°C [14]. The optical transmittance is continuous at the smectic-A to cholesteric transition. Here remarkably it is note that, the molecular orientation of this transition is not energetic. The optical transmittance decreases while on increasing the temperature and it diverges on approaching the cholesteric phase. The divergence of the optical transmittance is related to the first-order or second order transition. Here in the region of cholesteric phase, the optical transmittance becomes a steep decrease, which close to isotropic phase and it is the characteristic of first-order transitions of cholesteric phase respectively at different temperatures.

Electrical conductivity

Electrical-conductivity measurements help in getting better idea on the phase behavior with temperature. An abrupt increase or decrease of electrical-conductivity with temperature relates to the phase behavior of the lyotropic and thermotropic systems [15]. The temperature variations of electrical conductivity are shown in Fig. 8, which clearly illustrates that there is some change in the value of electrical conductivity from 37°C to 115°C, while cooling from isotropic phase for the mixture of 24% CL in (Naol + H_3PO_4). For the mixture of 24% CL in (Naol + H_3PO_4), the sequence of phase changes from Cho to SmG phase. Here, it has been found that the electrical conductivity goes on increasing as the temperature decreases. Significantly decrease in electrical conductivity evidenced the presence of the effect of positive temperature coefficient of resistivity. This suggests that aggregated molecular size starts growing toward lower temperatures and then the system becomes more ordered [16–21].

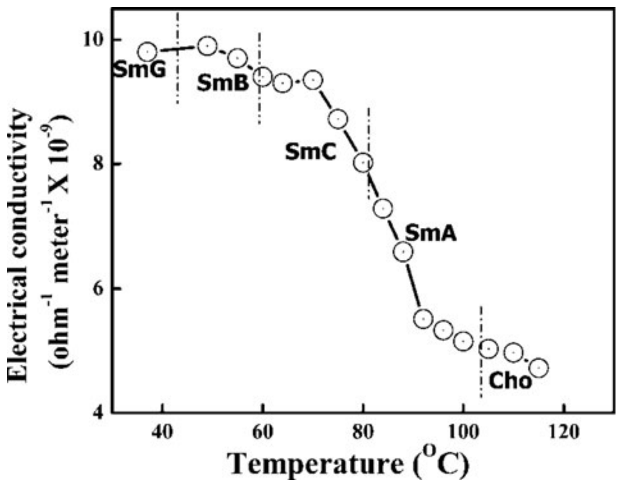


Figure 8. Temperature variation of electrical-conductivity σ ($\times 10^{-9}\ \Omega^{-1}\ m^{-1}$) for the sample of CL in (Naol + H_3PO_4).

Conclusion

Microscopic investigation of the binary/ternary mixture of CL in (Naol + H_3PO_4) shows the existence of Iso→Cho→SmA→SmC→SmB→SmG phases for all concentrations of given mixture. The phase behavior is discussed with the help of phase diagram. The drastic changes in the optical anisotropic measurements with variation of temperature unambiguously correspond to polymorphic smectic phases, respectively at different concentrations. The experimentally measured optical transmittance has been discussed based on the phase transition behavior of different temperature.

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