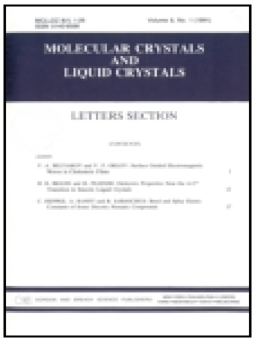

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T. N. Govindaiah & H. R. Sreepad

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Phase Diagram Involving Induced Smectic Phases in Binary Mixture of Two Liquid Crystals

T. N. GOVINDAIAH* AND H. R. SREEPAD

Post-Graduate Department of Physics, Government College (Autonomous), Mandya, India

*The binary mixture of cholesteryl oleate (CO) and 4′-*n*-octyl-4-cyanobiphenyl (8CB) exhibits interesting liquid crystalline mesophase cholesteric and induced smectic phases, such as SmA, SmC, SmB, and SmE, sequentially when the specimen is cooled from its isotropic liquid phase. These phases have been characterized by using differential scanning calorimetric and optical texture studies. The temperature variation of optical anisotropy and electrical conductivity has also been discussed.*

Keywords Temperature dependence; mesomorphic phases; optical texture studies; phase diagram

Introduction

Liquid crystals can be defined as systems where liquid like ordering exists at least in one dimension and where the particle density pair correlation function is not only dependent on the distance $|x - x_0|$ but also on the orientation of the vector $x - x_0$ [1]. In addition to being intermediate states, liquid crystals mesophases have physical properties inherited from both isotropic liquids and solid crystal materials. For example, Liquid crystals systems might have the ability to flow and the inability to resist stress (like an isotropic liquid) but also have the ability to transmit a torque (like a solid) [2].

Liquid crystalline systems can be roughly divided into two categories based on what acts as the driving force for phase transitions. In thermotropic liquid crystals, the driving force for phase changes is provided by changes in temperature. For example, on cooling a system can move from an isotropic liquid to a nematic liquid crystal mesophase with orientational order. In lyotropic liquid crystals the changes between different mesophases are driven by a change in the concentration in addition to temperature changes.

In nature self-organization is not only limited to liquid crystals, but is present in a wide variety of soft condensed matter systems [3, 4]. For example in a dib lock copolymer system, which is the simplest case of a general block copolymer, the incompatibility of the two building blocks leads to phase segregation and to a wide cascade of different self-organized mesophases [5]. Another example of self-organization is provided by amphiphilic molecules in solution. Amphiphilic molecules consist of hydrophobic

*Address correspondence to Dr. T.N. Govindaiah, Asst. Professor, P.G. Department of Physics, Government College (Autonomous), Mandya-571401, India. E-mail: tngovi.phy@gmail.com

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and hydrophilic parts [6]. In aqueous solution, with favorable concentration and temperature, surfactant molecules can self-assemble to form micelles and a range of lyotropic liquid crystalline mesophases. Another example of systems exhibiting lyotropic liquid crystalline behavior is rod like colloidal particles. For example colloidal suspension of Tobacco Mosaic virus will form liquid crystal phases at high concentration of particles.

In the present study, we have considered the mixture of two compounds viz., cholesteryl oleate (CO) and 4′-*n*-octyl-4-cyanobiphenyl (8CB). Some of the concentrations of the mixture exhibit Iso→Cho→SmA→SmC→SmB→SmE→Cryst phases sequentially when they are cooled from isotropic phase. Optical, thermal, and X-ray studies have been carried out to understand the intermolecular interactions in the mixture.

Experimental Section

In the present investigation, we have studied binary mixtures of liquid crystals, namely, cholesteryl oleate (CO) and 4′-*n*-octyl-4-cyanobiphenyl (8CB). Which are obtained from M/s Eastmann Organic Chemicals, USA. The chemicals are purified twice with benzene. Mixtures of twenty five different concentrations of CO in 8CB were prepared and were mixed thoroughly. These mixtures of various concentrations of CO in 8CB 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 differential scanning calorimetry (DSC) thermograms were taken for the mixtures of all concentrations using Perkin-Elmer DSC II Instrument facility available at Raman Research Institute, Bangalore, India. The X-ray broadening peaks were obtained at different temperatures using JEOL diffractometer. The density and refractive indices in the optical region are determined at different temperatures by employing the techniques described by the earlier investigators [6, 7]. Electrical-conductivity measurements of the mixture at different temperatures were carried out using digital LCR meter and a proportional temperature control unit.

Results and Discussions

Phase Diagram

The partial phase diagram shown in Figure 1, which clearly illustrates that mixtures with concentrations from 5% to 45% and 65% to 90% of CO in 8CB exhibit an interesting cholesteric, SmA, SmC, SmB, and SmE phases sequentially when the specimen is cooled from its isotropic melt. But in the concentrations range from 46% to 64% of CO in 8CB shows a only induced smectic phases such as SmA, SmC, SmB, and SmE respectively at different temperature. The isotropic liquid region to crystalline region, the phase transition temperature increases on increasing the concentration of CO. The phase behavior is discussed with the help of phase diagram (Figure 1) [8].

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

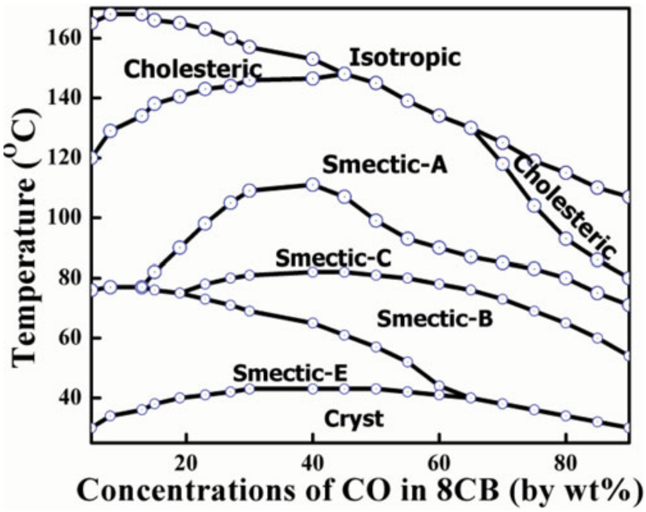

Figure 1. Partial phase diagram for the mixture of CO in 8CB.

in conjunction with specially constructed hot stage. The concentrations ranges from 5% to 45% 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 fingerprint pattern of cholesteric phase with large values of pitch [9, 10]. On further cooling the specimen, the cholesteric phase slowly changes over to focal conic fan shaped texture, which is the characteristics of SmA phase as shown in Figure 2(a). On further cooling the specimen, SmA phase changes over to schlieren texture of SmC phase, which as shown in Figure 2(b). The SmC phase is unstable and then this phase changes over to broken banded texture of SmB phase. On further cooling the specimen, the SmB phase changes over to SmE phase, which remains up to room temperature, and then it becomes a crystalline phase.

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 27% of CO in 8CB are as shown in Figure 3. The value of n_e is greater than n_o, indicating that the material is uniaxial positive. The values of electrical susceptibility for 27% of CO in 8CB have been calculated using Neugebauer relation [11] at different temperatures. The temperature variations of electrical susceptibility for the mixture are as shown in Figure 4. 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. Further, with increase in the concentration of CO, the value of electrical susceptibility decreases with temperature, because the effective optical anisotropy associated with the molecules of CO also decreases.

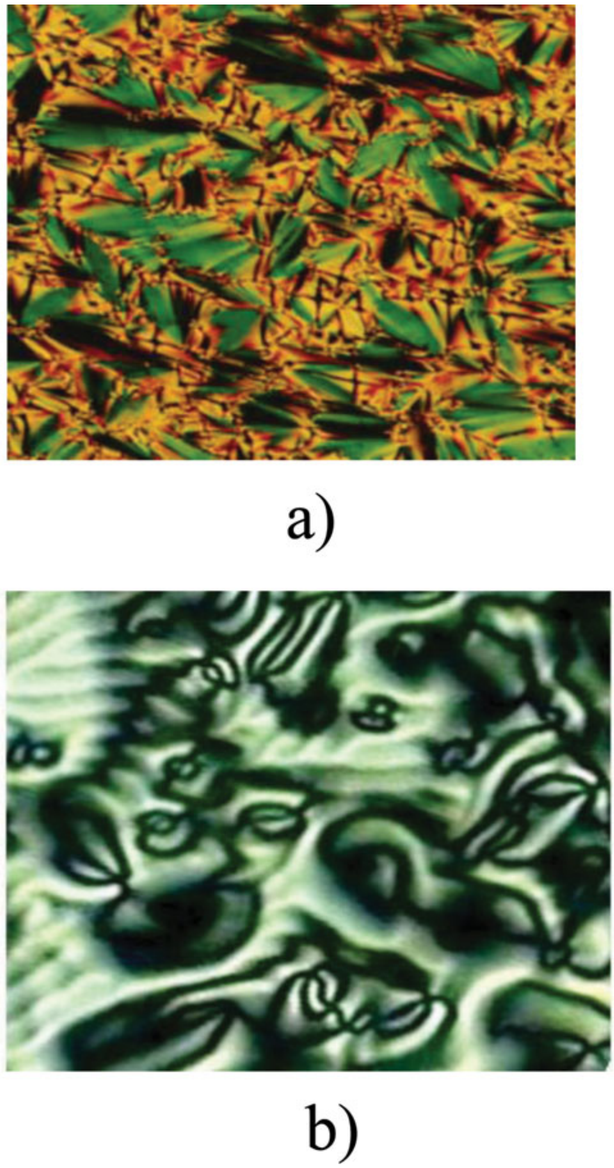

Figure 2. Microphotographs obtained in between the crossed polars, a) Focal conic fan shaped texture of SmA phase (250×). b) Schlieren texture of SmC phase (250X).

Conductivity Measurements

Electrical-conductivity measurements are helpful in the study of phase behavior with temperature. An abrupt increase or decrease of electrical-conductivity with temperature relates to the phase behavior of the lyotropic system [12]. The temperature variations of electrical-conductivity are shown in Figure 5. The changes were observed in electrical-conductivity, that values corresponds to smectic and cholesteric phase transitions of the thermotropic

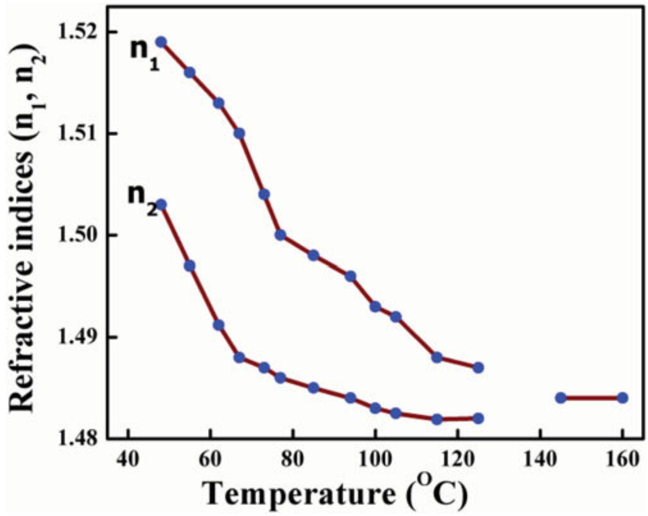

Figure 3. Temperature variations of refractive indices for the mixture of 27% CO in 8CB.

and lyotropic system at various temperatures and they were also identified by optical texture studies. It was observed that an abrupt change in electrical-conductivity at different temperatures, respectively, which corresponds to the phase transition from to crystalline phase. This type of behavior is generally observed in hexagonal, cubic and lamellar phase of lyotropic and thermotropic systems [13, 14].

Conclusions

In light of the above results, we have drawn the following conclusions. The binary mixture of CO in 8CB exhibits an conventional different liquid crystalline phases, showing the

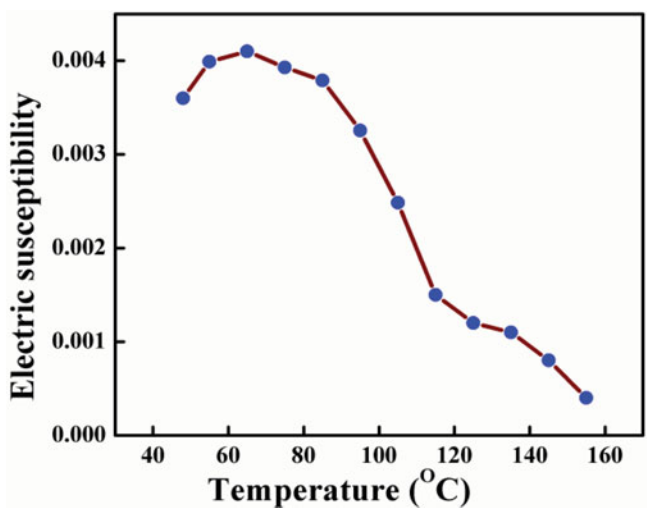

Figure 4. Temperature variation of electrical susceptibility for the mixture of 27% CO in 8CB.

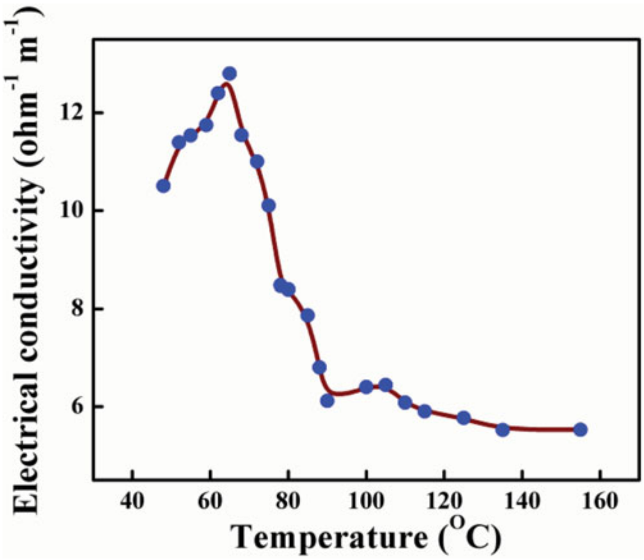

Figure 5. Temperature variation of electrical-conductivity σ (Ω^{-1} m^{-1}) for the sample 27% CO in 8CB.

formation of cholesteric and induced smectic phase at different concentrations of given mixture, respectively, at temperature. 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.

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