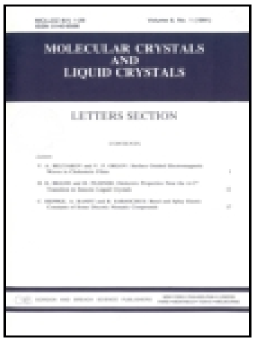

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# Studies on Optical Characterization and Nano-Aggregation of Molecules in Ternary Mixture of Liquid Crystalline Materials

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*Two or more multicomponents system of cholesteryl ethyl corbonate, didodecyl dimethyl ammonium bromide, and ethylene glycol exhibits liquid crystalline phase of cholesteric and induced smectic phases, such as SmA, SmC, SmC*, and SmE, sequentially when the specimen is cooled from isotropic liquid phase. These phases have been characterized by using X-ray and optical texture studies. The temperature variation of optical anisotropy and electrical conductivity has also been discussed.*

**Keywords** Mesomorphic phases; nano-aggregation; optical texture studies; phase diagram; temperature dependence

## Introduction

Lyotropic systems give spectacular examples of polymorphism and phase transformations depending on changes of temperature, pressure, and other physico-chemical parameters. The use of amphiphilic molecules in everyday life was originally due to the empirical properties of mixtures of these molecules with polar and nonpolar solvents. In the last decades, however, there was an enormous improvement of experimental techniques, as the scattering and diffraction of light, neutrons, and X-rays, nuclear magnetic resonance, electron microscopy and fluorescence, atomic force microscopy, and nonlinear optical techniques, which are among the most powerful tools of condensed matter physics. These techniques lead to the establishment of additional and more precise information on the structure, local ordering, and phase transitions of the phase diagrams of lyotropic mixtures [1].

The discovery of a nematic phase in a lyotropic mixture of sodium decylsulfate and water, by Lawson and Flautt, opened up the opportunity to use similar concepts for analyzing different sorts of liquid crystalline systems, thermotropics, and lyotropics [2].

Lyotropic liquid crystals, shortly called lyotropics, are mixtures of amphiphilic molecules and solvents at given temperature and relative concentrations. The mesomorphic

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properties change with temperature, pressure, and the relative concentrations of the different components of the mixture [3]. An important feature of lyotropics, turning them different from thermotropics, is the self-assembly of the amphiphilic molecules as supermolecular structures, which are the basic units of these mesophases. Although there are not many devices based on lyotropics, their physico-chemical properties have an interesting interface with biology, and the understanding of these properties has been relevant for improving some technological aspects of cosmetics, soaps, food, crude oil recovery, and detergent production.

In the present investigation, our aim is to study the mixture of multicomponent system, namely, cholesteryl ethyl corbonate (CEC), didodecyl dimethyl ammonium bromide (DDAB), and ethylene glycol (EG) which exhibits liquid crystalline cholesteric and induced smectic phases, such as SmA, SmC, SmC*, and SmE phases, respectively, at different temperatures. They were observed using microscopic technique and also have been verified from the results of X-ray and optical anisotropic techniques.

## Experimental Section

The compound DDAB 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. EG was supplied from Kodak, Ltd., Kodak house, Mumbai, India. The CEC was obtained from M/s East Mann Organic Chemicals, USA. Mixtures with different concentrations of CEC in DDAB + EG were prepared and were mixed thoroughly. These mixtures of various concentrations of CEC in DDAB + EG 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 X-ray peaks were obtained by 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 [4, 5]. The electrical conductivity measurements for given mixture at different temperatures were carried out using digital LCR meter and a proportional temperature control unit.

## Results and Discussions

### *Phase Diagram*

The ternary mixture of CEC in (DDAB + EG) exhibits different liquid crystalline phases and the phase transition temperatures are measured by using Leitz-polarizing microscope. The partial phase diagram is as shown in Fig. 1. This is obtained by plotting the concentrations against the phase transition temperatures of the mixture. This clearly illustrates that, the mixture with concentrations ranging from 5% to 50% of CEC in (DDAB + EG) exhibits Cho, SmA, and SmE phases, respectively, at different temperatures, when the specimen is cooled from isotropic phase. Mixture with concentrations ranging from 5% to 27% and 18% to 50% of CEC molecules exhibit chiral smectic phases such as SmC and SmC*, respectively, at different temperatures [6].

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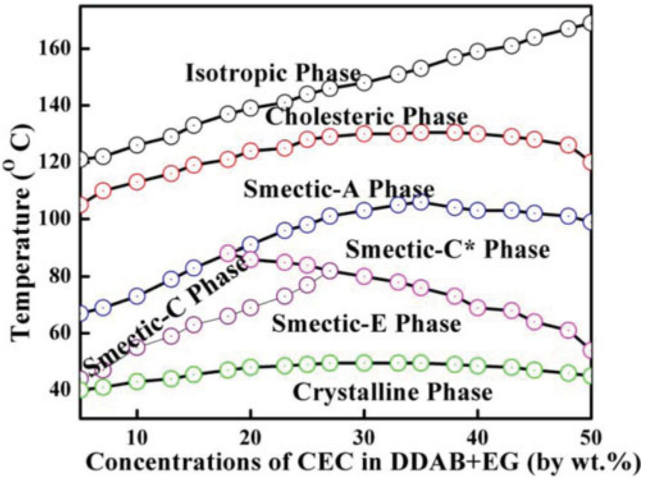

**Figure 1.** Partial phase diagram for the mixture of CEC in (DDAB + EG).

### Optical Texture Studies

For the purpose of optical texture studies, the sample was sandwiched between slide and cover glass and then the optical textures were observed using a Leitz polarizing microscope in conjunction with a specially constructed hot stage. Mixtures with concentrations ranging from 18%–27% of CEC in (DDAB + EG) slowly cooled from isotropic melt. The genesis of nucleation starts in the form of small bubbles and slowly grows radially, which forms a fingerprint pattern of cholesteric phase with large values of pitch is shown in Fig. 2(a) [7, 8]. On further cooling, the cholesteric phase slowly changes over to focal conic fan-shaped texture, which is the characteristic of SmA phase and is as shown in Fig. 2(b). The SmA phase is not stable and then changes over to SmC* phase, which exhibits radial fringes on the fans of focal conic textures, which is characteristic of chiral SmC* phase. Further cooling the specimen, the chiral SmC* phase changes over to schlieren texture of SmC phase as shown in Fig. 2(c). On further cooling, this phase changes over to the crystalline SmE phase, which remains up to room temperature and then it becomes crystalline phase.

### Characterization of Nano-Aggregated Grains

The X-ray diffraction traces obtained for the mixture of 23% of CEC in (DDAB + EG) at temperature 65 °C is shown in Fig. 3. The diffraction peaks at this temperature correspond to smectic-E phase (by using JEOL diffractometer with the settings: TC4, CPS400, channel width 100 for $\lambda = 1.934$ Å). X-ray diffraction study is an important method to determine the nano-aggregated grain size of the molecules for different liquid crystalline phases [9, 10]. The X-ray traces obtained for the Perfect liquid crystals would extend in all directions to infinity, so we can say that no crystal is perfect due to its finite size. The deviation from perfect liquid crystallinity leads to a 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 Scherer's formula

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

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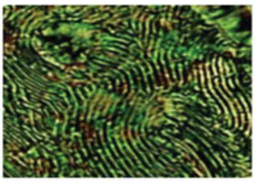
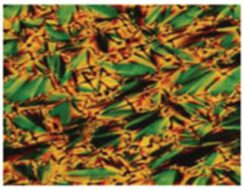


a). Fingerprint pattern of cholesteric phase (250X).



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

c). Schlieren texture of SmC phase (250X).

**Figure 2.** Microphotographs obtained in between the crossed polars.

where *L* is the nano-aggregated grain size, λ is the wave length of X-ray radiation (1.934 Å), *K* is usually taken as 0.89, *β* is the line width at half maximum, and *θ* is the diffraction angle. With decrease of temperature [11, 12], the nano-aggregated grain size of the molecules increases. In Fig. 3, we have observed that, the structure of molecular

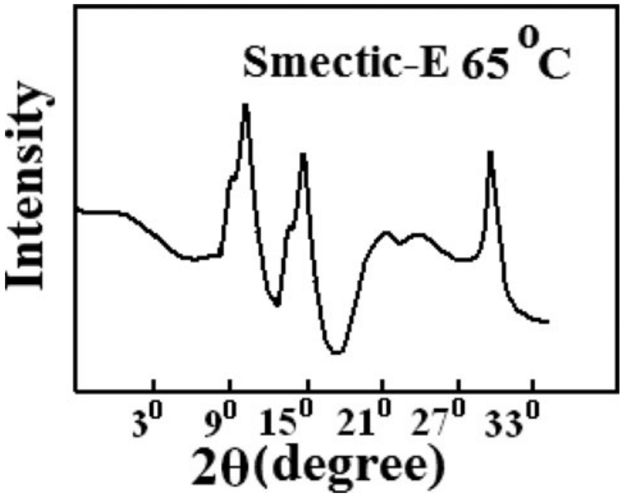


**Figure 3.** XRD traces obtained for the mixture of 23% of CEC in (DDAB + EG).

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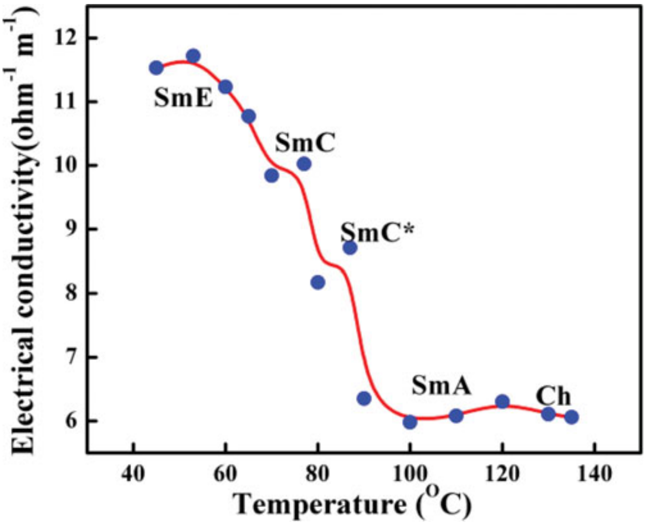

**Figure 4.** Temperature variation of electrical-conductivity $\sigma$ ($\Omega^{-1}$ m$^{-1}$) for the sample 23% of CEC in (DDAB + EG).

orientation for herringbone pattern of smectic-E phase is energetically more stable and molecular ordering of this phase shows three intense peaks. The nano-aggregated grain size of liquid crystalline material for smectic-E phase is estimated to be 46.8 nm. From this study, we have observed that, the molecular ordering of liquid crystalline materials is increasing as we move toward lower temperature. This clearly illustrates that, nano-aggregated grain size of liquid crystalline materials of different phases are big enough to indicate that the molecular ordering [13] of layer structure increases with decrease in the temperature.

## 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 relates to the phase behavior of the lyotropic and thermotropic systems [14]. The temperature variation of electrical-conductivity is shown in Fig. 4. The changes were observed in electrical-conductivity, the values correspond to liquid crystalline phase transition of thremotropic and lyotropic systems, respectively, at different temperatures and they were also identified by optical texture studies. It was observed that, the electrical-conductivity shows changes as we move from 132°C →100°C, 100°C →80°C, 80°C →70°C, and 70°C →53°C, which correspond to phase transitions Ch→ SmA, SmA→ SmC*, SmC*→ SmC, and SmC→ SmE phases respectively. This type of behavior is generally observed in hexagonal, cubic and lamellar phases of lyotropic and thermotropic systems [15, 16]. These abrupt changes cannot be throughout if only due to change in the orientation of molecules. They can be attributed to changes in the dimension of disk along with changes in orientation.

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## Conclusions

In light of the above results, we have drawn the following conclusions. The multicomponent system exhibits different liquid crystalline phases, showing the formation of cholesteric and induced chiral smectic phases in the concentrations ranging from 5%–50% of CEC in (DDAB + EG), respectively, at different temperatures. The phase behavior has been 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 disc along with changes in the orientation order of the arrangement. X-ray and optical studies also lend support to these observations. The nano-aggregated grain size of liquid crystalline material for smectic-E phase comes out to be 46.8 nm.

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