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Phase transition and thermal characterization of induced smectic phases in a ternary mixture

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ABSTRACT

Two or more multi-component system of didodecyl dimethyl ammonium bromide (DDAB), cholesteryl nonanoate (CN) and ethylene glycol (EG) exhibits an interesting different liquid crystalline cholesteric and induced smectic phases, such as SmA, SmC and SmB, sequentially when the specimen is cooled from its isotropic liquid phase. These phases have been characterized by using optical texture studies. The temperature variations of optical anisotropy, helical pitch measurements and electrical conductivity have been also discussed. XRD results have also been reported.

1. Introduction

Liquid crystals are a special class of soft materials characterized by so called mesophase, where they flow like an isotropic liquid yet possess a long-range orientational order and a complete or partial absence of positional order of building units that can either be individual molecules or their aggregates [1]. The two main types of liquid crystals are thermotropic liquid crystals and lyotropic liquid crystals. Thermotropic liquid crystals show mesophases depending on temperature and pressure. Their basic building units are usually individual molecules that have a feature of pronounced shape anisotropy, such as rods and disk. Thermotropic liquid crystals have been successfully used in display devices. Lyotropic liquid crystals are formed on the dissolution of lyotropic liquid crystal molecules in a solvent (usually water). A feature of lyotropic liquid crystals distinguishing them from thermotropic liquid crystals is the self-assembly of molecules into supramolecular structures that represent a basic unit of these mesophases [2,3].

The most common lyotropic liquid crystalline system is those formed by water and surfactants, such as soaps, synthetic detergents, and lipids. Surfactant molecules are formed by a hydrophilic part chemically bound to a hydrophobic part. Mixtures of these surfactant molecules with a solvent under certain conditions of temperature and relative concentrations produced the different types of liquid crystalline mesophases such as cholesteric, nematic, lamellar, discotic, twisted grain boundary (TGB) phase, and blue phase [4].

In the present investigation, our aim is to study the ternary mixture of different compounds, namely, cholesteryl nonanoate (CN), Didodecyl dimethyl ammonium bromide (DDAB) and ethylene glycol (EG), which exhibits an interesting liquid crystalline cholesteric phase and induced smectic phases, such as SmA, SmC and SmB phases sequentially when they are cooled from isotropic phase. Optical, DSC, thermal and X-ray studies have been carried out to understand the intermolecular interactions in the mixture.

2. Experimental

The compound didodecyl dimethyl ammonium bromide (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. Ethylene glycol (EG) was supplied from Kodak, Ltd., Kodak house, Mumbai, India. The cholesteryl nonanoate (CN) was obtained from M/s East Mann Organic Chemicals, USA. Mixtures of different concentrations of DDAB in CN + EG were prepared and were mixed thoroughly. These mixtures of various concentrations of DDAB in CN + 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 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

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and refractive indices in the optical region are determined at different temperatures by employing the techniques described by the earlier investigators [5,6]. Electrical-conductivity measurements of the mixture at different temperatures were carried out using digital LCR meter and a proportional temperature control unit.

3. Results and discussion

3.1. Phase diagram

The ternary mixture of DDAB in CN + EG exhibits an interesting different liquid crystalline phases and the phase transition temperatures are measured by using Leitz-polarizing microscopic. The partial phase diagram shown in Fig. 1, which is obtained by plotting the concentrations against the phase transition temperatures of the mixture, which clearly illustrates that, the mixture of all concentrations of DDAB in CN + EG exhibit a SmA and SmB phases respectively at different temperatures, when the specimen is cooled from its isotropic liquid phase. The concentrations of the mixture from 5% to 22% and 32% to 60% of DDAB shows a cholesteric phase in addition of SmA, SmC and SmB phases, but in the concentration range from 8% to 50% of DDAB shows a schlieren texture of SmC phase.

3.2. Optical texture studies

For the purpose of optical texture studies, the sample was sandwiched between a slide and cover glass, and then the optical textures were observed using a Leitz polarizing microscope in conjunction with a specially constructed hot stage. The concentrations ranges from 5% to 22% and 32% to 60% of the 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 texture of cholesteric phase with large values of pitch is shown in Fig. 2(a) [7,8]. 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 Fig. 2(a). The concentrations from 8% to 50% of the mixture, the SmA phase changes over to schlieren texture of SmC. On further cooling the specimen, SmC phase changes over to SmB phase, which remains up to room temperature and then it becomes a crystalline phase [9].

3.3. 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 the different concentrations using Abbe refractometer and precision goniometer spectrometer. The temperature variations of refractive indices

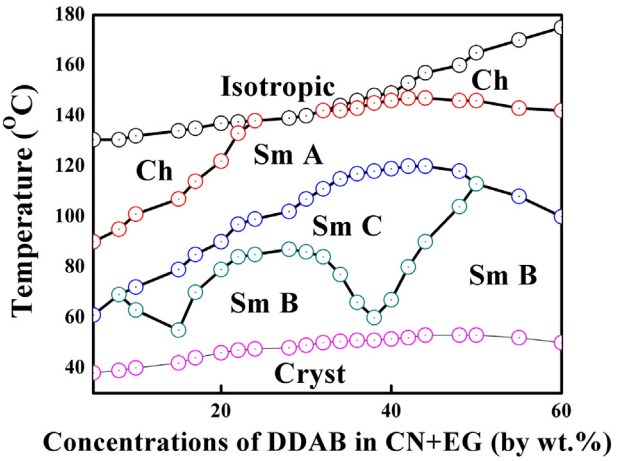
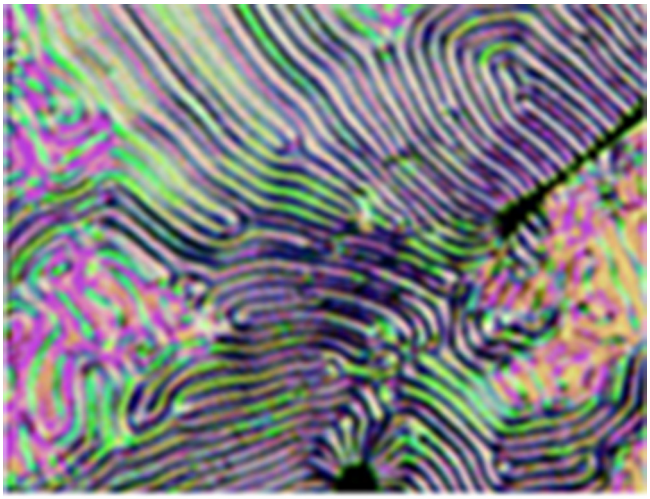
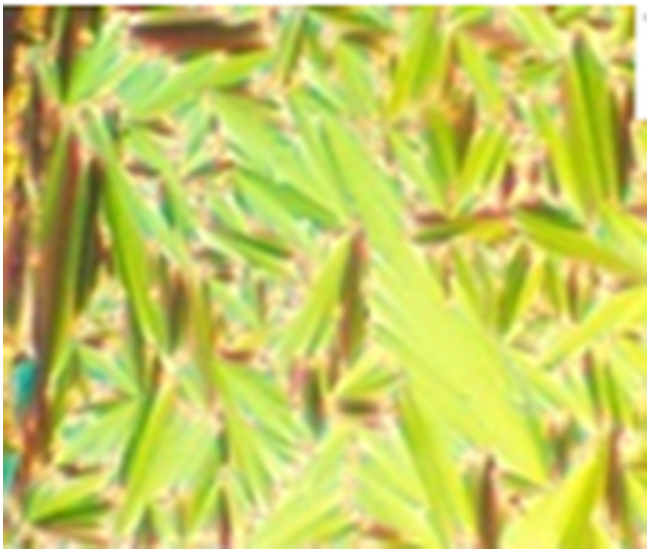


Fig. 1. Partial phase diagram for the mixture of DDAB in CN + EG.



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



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

Fig. 2. Microphotographs obtained in between the crossed polars. a). Fingerprint pattern texture of cholesteric phase (250×). b). Focal conic fan shaped texture of SmA phase (250×).

for 20% of DDAB in CN + EG are shown in Fig. 3. The values of electrical susceptibility for 20% of DDAB in CN + EG have been calculated using Neugebauer relation [10] at different temperatures. The temperature variations of electrical susceptibility for the mixture are as shown in Fig. 4. From this figure, it can be observed that wherever there is a phase transition, the value of electrical susceptibility changes appreciably, which indicates that each change corresponds to induced mesomorphic phases. Further with increasing the temperature of given concentration of DDAB, the value of electrical susceptibility decreases, because the effective optical anisotropy associated with the molecules of DDAB also decreases. But here in this graph, we have observed an auxiliary peak in addition to the main peak, which illustrates that, the peak cannot be thought only due to change in the orientation of molecules. They can be attributed to changes in the dimension of molecules along with changes in orientation.

3.4. Helical pitch (smectic and cholesteryl layers) measurements

The helical pitch measurements were performed on the cholesteric phase following the well-known Grandjean–Cano wedge method [11,