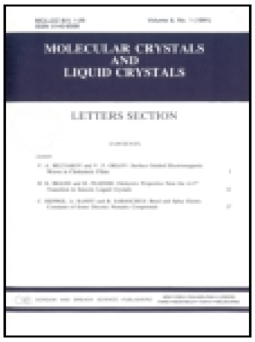
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Induced Polymorphism of Smectic Phases in Binary Mixture of Liquid Crystals

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The binary mixture of two nonmesogenic compounds viz., DTAC and EG exhibits very interestingly induced polymorphism of smectic phase's at large range of concentrations with temperature. The mixture with range of concentrations below 50% of DTAC exhibits SmA, SmC, SmC SmE, and SmB phases, sequentially when the specimen is cooled from its isotropic phase. Different liquid crystalline phases observed in the mixture were studied using DSC, X-ray, and Optical microscopic techniques. The temperature variations of optical anisotropy and electrical conductivity have also been discussed.*

Keywords Binary mixture; binary mixture; nonmesogenic, phase transition; smectic

Introduction

Liquid crystals are very important materials because of their technological importance, but a single liquid crystal material cannot fulfill all the requirements for a practical device. Therefore, the different mixtures of liquid crystals and their doped samples have gained growing interest. These doped samples have emerging prospects regarding their applications in information processing [1].

Thermotropic liquid crystals are materials possessing one or more mesophases between the isotropic liquid and the solid phase. The mesophase sequence, observed when the temperature is changed, is due to a sequential ordering of molecular arrangements. The shape of molecules is then fundamental to determine the features of this sequence. For rod-like molecules, the material can achieve a nematic phase characterized by an orientational order of molecules. In the smectic phases, the order increases: besides the orientational order, the molecules have an arrangement in layered structure, in some cases with tilt (smectic C) or positional order within the layers (for instance in smectic B) [2–5]. Being strongly anisotropic materials, with optical birefringence properties, a technique commonly applied to detect the material order is the polarized light microscopy, using sandwich cells typically with thickness from 10 to 100 microns. The temperature-driven phase transitions are the most beautiful phenomena that can be observed, with sudden changes of colors and textures and very rich in pattern formation.

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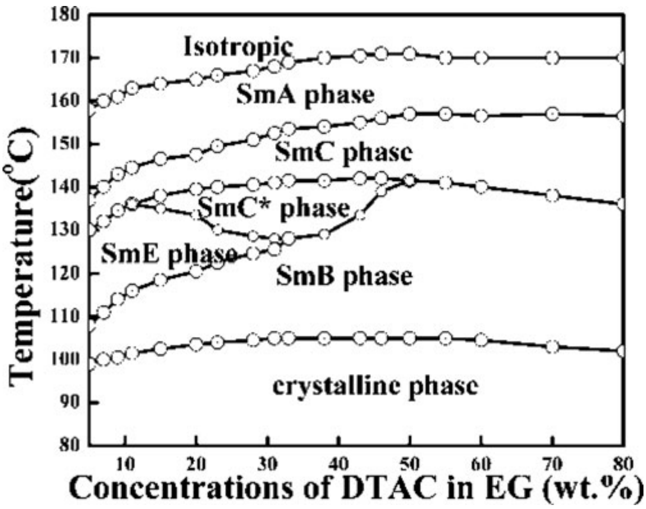

Figure 1. Partial phase diagram for the mixture of DTAC in ethylene glycol (EG).

In the present study, we have considered the mixture of DTAC and EG molecules. The polymorphic smectic liquid crystalline phases were observed using microscopic technique and they have been also verified from the results of X-ray and Optical anisotropic techniques.

Experimental Section

The compound DTAC used in this investigation was obtained from the Basic Pharma Life Science Pvt., Ltd., India, and it was further purified twice by a re-crystallization method using benzene as a solvent. EG was supplied from Kodak, Ltd., Kodak house, Mumbai, India. Mixtures of different concentrations of DTAC in EG were prepared and were mixed thoroughly. These mixtures of various concentrations of DTAC in 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 and refractive indices in the optical region are determined at different temperatures by employing the techniques described by the earlier investigators [6, 7].

Results and Discussion

Phase Diagram

Mixture of DTAC in 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. 1, and it is obtained by plotting the concentrations

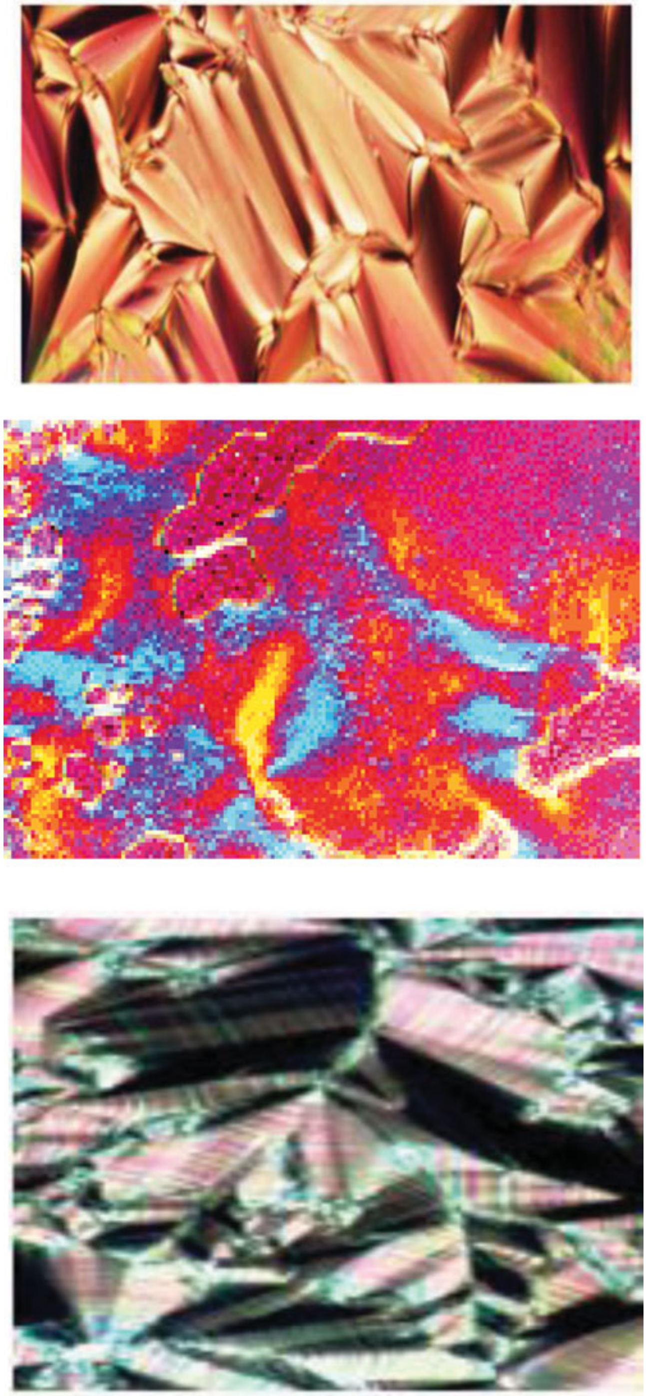

Figure 2. Microphotographs obtained in between the crossed polars, (a) Focal conic fan-shaped texture of SmA (Lamellar) phase (250×). (b) Schlieren texture of chiral Sm C phase (180×). (c) Focal conic fans with radial striation of smectic-E phase (250×).

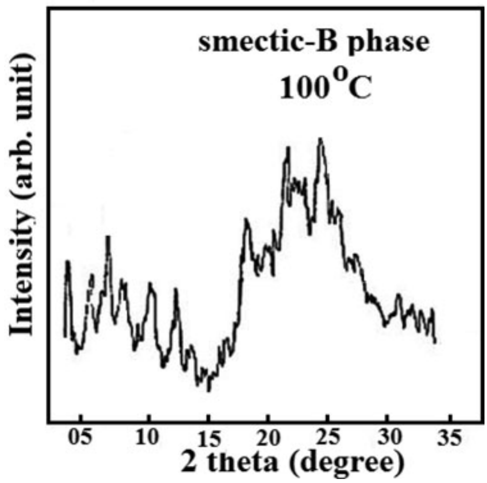

Figure 3. XRD traces obtained for the mixture 23% of DTAC in ethylene glycol (EG) at temperature 100 °C.

against the phase transition temperatures of the mixture, which clearly illustrates that the mixture of all concentrations of DTAC in EG exhibits an induced polymorphic smectic phases, such as SmA, SmC, 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 11% to 50% of DTAC show an unusual chiral SmC* phase, but in the range from 5% to 33% of DTAC shows an SmE phase. All concentrations range from 5% to 80% of DTAC shows SmB phase, which remains up to room

Optical Texture Studies

The optical textures exhibited by the samples were studied using the Leitz-polarizing microscope and specially constructed hot stage. The specimen was taken in the form of thin film and sandwiched between the slide and cover slip. The concentrations from 5% to 80% of mixture of lyotropic liquid crystals have been considered for the experimental studies. When the specimen of 25% DTAc is cooled from isotropic liquid phase, it exhibits

Table 1. X-Ray data of 23% DTAC in EG at 100°C temperature

h	*k*	1	2θ (obs)	2θ (cal)	Cell parameter
1	0	1	4.235	4.236	a = 20.2180 Å
2	1	0	6.370	6.360	b = 16.9870 Å
2	1	1	7.110	7.120	c = 5.33920 Å
2	1	3	13.370	13.371	α = 90.000 D
3	2	1	18.101	18.100	β = 90.000 D
2	4	1	22.673	22.674	γ = 90.000 D
5	4	0	25.486	25.487	
Unit cell Volume = 1947.74A^3					

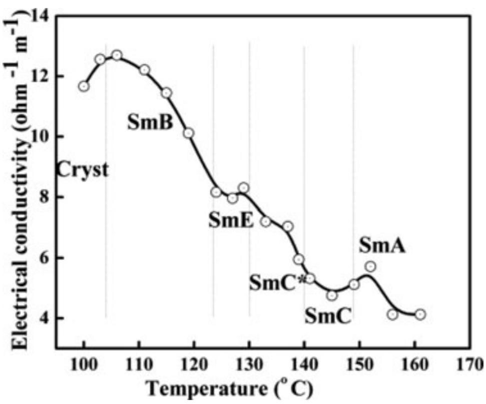

Figure 4. Temperature variation of electrical-conductivity σ (Ω^{-1} m^{-1}) for the sample 23% of DTAC in ethylene glycol (EG).

and Iso—Sm A—Sm C*—Sm E—Sm B—Cry phases. While the sample is cooled from isotropic liquid phase, the genesis of nucleation starts in the form of small bubbles grows radially which were identified as focal conic fan texture of Sm A phase as shown in the Fig. 2 (a). The Sm A phase change over to schlieren texture as shown in the Fig. 2(b), which is the characteristic of Sm C phase. On further cooling the specimen, Sm C phase change over to SmC* phase, which exhibit a radial fringes on the fans of focal conic textures, these are the characteristics of chiral SmC*phase. On further cooling, the SmC* phase changes over to SmE phase shown in Fig. 2(c) and then it change over to SmB phase, which remains up to room temperature and then it becomes a crystalline phase.

X-ray Studies

The X-ray recording has been obtained for the mixture of 23% DTAC in EG at the temperature of 100 °C, as shown in Fig. 3, and the recordings at this temperature, respectively, correspond to the SmB phase. Peaks obtained in XRD traces reveal that the reflections are corresponding to the SmB phase. The cell parameters are obtained by trial and error method. Here, the program starts with an initial set of parameters (a, b, c, α, β, Υ) and refines this set of parameters until all the observed X-ray reflections (h, k, l) are identified. The parameters obtained are given in Table 1 and it gives the volume of unit cell as 1947.74A^3, which is the approximated volume of the micelles.

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 [8]. The temperature variations of electrical-conductivity are shown in Fig. 4. 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 104°C, 123°C, 130°C, 140°C, and 149.5°C, respectively, which corresponds to phase transition from SmB to SmE, SmE to

SmC*, SmC* to SmC phase, and SmC to SmA. This type of behavior is generally observed in hexagonal, cubic, and lamellar phase of lyotropic and thermotropic systems [9,10].

Conclusions

The above studies apart from revealing numerous textures associated with various phases in mixture have enabled us to reach the following conclusions. Mixture with concentrations from 5% to 80% of DTAC in EG exhibits induced polymorphic smectic modifications at different temperatures. The drastic changes in the values of density, refractive index, and anisotropy of polarizability with temperature unambiguously correspond to smectic-B phase. The X-ray results also lend support to the above observations.

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