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Formation of Molecular self assembly of Polymorphic Lytropic Induced Chiral Smectic Phases in Binary Mixtures of Liquid Crystalline Materials

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Abstract

The binary mixture of two non-mesogenic compounds viz.,Voriconzole and ethylene glycol (EG) exhibits very interesting liquid crystalline phase's at large range of concentrations and temperature. The concentrations with lower/higher percentage of Voriconzole exhibit polymorphic lyoropic induced chiral smectic phases, such as SmA, SmC, SmC* and SmE phases, sequentially when the specimen is cooled from its isotropic liquid phase. Different liquid crystalline phases observed in the mixture were studied by using X-ray and Optical microscopic techniques. The temperature variations of optical anisotropy have also been discussed.

Keywords: Molecular self assembly; Induced chiral smectic phase; Optical anisotropy: X-ray studies:

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INTRODUCTION

Comprehensive studies on the mesomorphic behavior of mixtures of non mesogenic compounds have been well investigated [1-5]. Binary mixtures of some non mesogenic compounds exhibit lyotropic and thermotropic mesophases [6, 7]. Generally, the chemical structure is the most salient feature of molecules forming lyotropic mesophases in the presents of solvent. It is quite interesting to investigate the molecular self assembly of lytropic mesophases formed by organic solvent system.

In the present investigation, our aim is to study the binary mixture of non-mesogenic compounds, namely, Voriconzole and ethylene glycol (EG), which exhibits polymorphic lyoropic induced chiral smectic phases, such as SmA, SmC, SmC* and SmE phases, sequentially when the specimen is cooled from its isotropic liquid phase. They were observed using microscopic technique and also been verified from the results of optical anisotropic techniques. The X-ray studies have been used to show the grain size of the given liquid crystalline materials. The electrical conductivity measurements have also been discussed.

EXPERIMENTAL STUDIES

In the present work we have been considered the compounds namely, Voriconzole, and Ethylene Glycol was obtained from the Padmashri Scientific, Mysore. It was further purified twice by a re-crystallization method using benzene as a solvent. Mixtures of different concentrations of Voriconzole, and Ethylene Glycol were prepared and were mixed thoroughly. These mixtures of various concentrations of Voriconzole, and Ethylene Glycol 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 broadening peaks were obtained using JEOL diffractometer. The refractive indices in the optical region are determined at different temperatures by employing the techniques described by the earlier investigators [8-10]. Electrical conductivity measurements of the given mixture at different temperatures were carried out using digital LCR meter and a proportional temperature control unit. [11, 12].

RESULTS AND DISCUSSIONS

PHASE DIAGRAM

The partial phase diagram is a very important method to determine the stability of liquid crystalline phase at different temperatures for different concentrations of the liquid crystalline materials. The partial phase diagram in the present case is as shown in Figure 1.

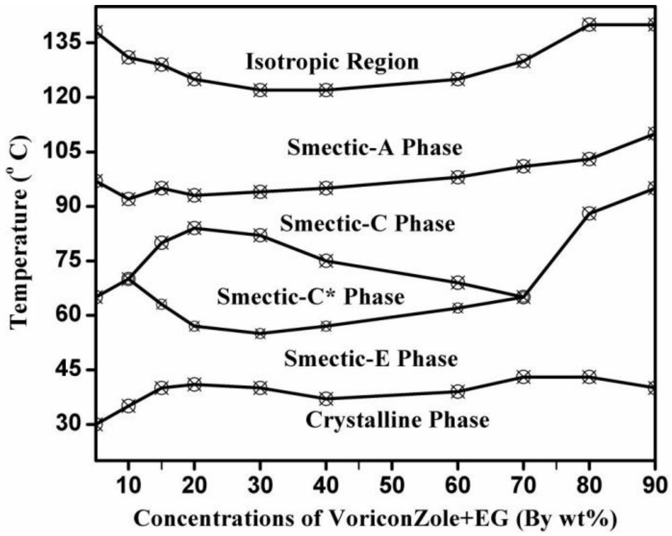


Figure 1. Partial phase diagram for the mixture of VoriconZole and Ethylene Glycol.

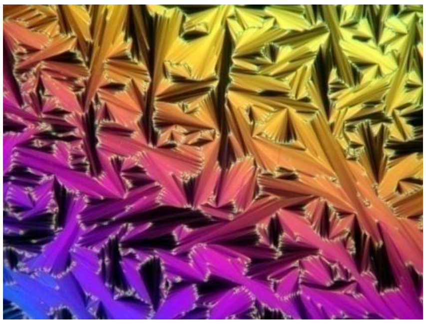
This clearly illustrates that mixtures with the concentrations ranging from 5% to 10% and 70% to 90% of VoriconZole and Ethylene Glycol exhibit Smectic-A, Smectic-C and Smectic-E phases, sequentially when the specimen is cooled from its isotropic melt. But the mixtures with concentrations of VoriconZole and Ethylene Glycol ranging from 10% to 70% of given mixture clearly shows a Smectic-C* phase in addition to mentioned above phases at different temperatures and at different concentrations. The phase diagram clearly shows polymorphic induced chiral smectic such as Smectic-A, Smectic-C, Smectic-C* and Smectic-E phases [13-15].

OPTICAL TEXTURE STUDIES

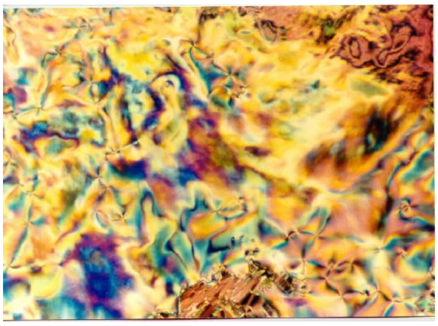
The polymorphic lyoropic induced chiral smectic modifications and the corresponding isotropic to liquid crystalline phase transition temperatures for the mixture with 40% of VoriconZole and Ethylene Glycol are given below.

Iso-122 ^{0}C, SmA-95 ^{0}C, Sm C-75 ^{0}C, SmC*-57 ^{0}C, SmE-37 ^{0}C.

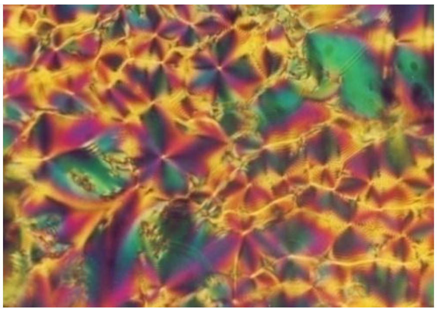
On cooling the specimen from its isotropic melt, the setting point is marked by the genesis of nucleation at several points which appear as minute bubbles initially, but which progressively grow radially and form a focal conic fan texture of smectic-A phase in which the molecules are arranged in layers and the texture is shown in Figure. 2 (a). This phase appears to be metastable and undergoes slow transformations to give schlieren texture of smectic-C phase as shown in Figure 2 (b) on cooling the specimen. The molecular orientation of SmC phase is not energetically stable and then it changes over to SmC* phase, which exhibits a radial fringes on the fans of focal conic textures, these are the characteristics of chiral SmC∗ phase, which as shown in Figure. 2 (c). In the same way, orientation of the molecules in SmC∗ phase is also not stable and then changes over to focal conic fan texture with radial striation on the fans [16,17], which is the characteristics of Smectic-E phase and it is observed as shown in Figure 2 (d).



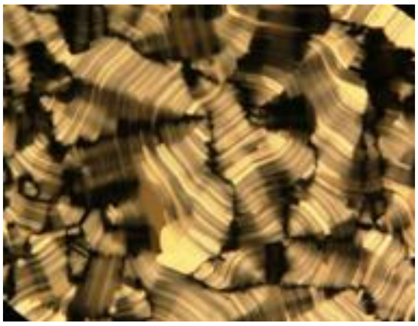
(a) Focal conic fan-shapedtexture of SmA phase at temperature 150^0C (250X).



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



(c) Radial fringes on the fans of focal conic textures of smectic-C* phase (250X).



(d) Focal conic fans with radial striation of smectic-E phase (250X).

Figure 2: Microphotographs obtained in between the crossed polars.

At this phase transition, i.e, from smectic-C* phase to smectic-E phase, it is observed that there is a drastic change in the values of refractive index and electro-conductivity of the sample [18, 19]. This anomalous behavior is presumably associated with the degree of order of the molecular arrangement in smectic-E phase and then it becomes crystalline phase at room temperature.

OPTICAL ANISOTROPIC STUDIES

Liquid crystal display has been commonly used in direct-view, e.g., cellular phones, notebook and desktop computers, and televisions, and large screen projection displays [20, 21]. The fundamental light modulation mechanism of a Liquid crystal display is electric field-induced molecular reorientation which, in turn, causes refractive index change. The refractive indices of a liquid crystal are mainly determined by the molecular structure, wavelength and operating temperature. To achieve a full-color display three primary colors (red, green, and blue) are needed. As the wavelength increases, the refractive indices decrease. The decreasing rate depends on the liquid crystal molecular structures. On the other hand, for a front or rear projection display, the thermal effect originated from the lamp heating raises the liquid crystal panel temperature to lower temperature. To design the liquid crystal panels for projection displays, we need to know the intended operating temperature. As on temperature increases, the extraordinary refractive index decreases monotonously, but the ordinary refractive index could decrease or increase depending the crossover temperatures of the liquid crystal employed. Therefore: the wavelength and temperature dependent refractive indices are fundamentally interesting and practically important for optimizing the display performances and other photonic devices employing liquid crystals.

Results of the present studies are further supported by the optical studies [22, 23]. 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. The variations of refractive indices as a function of temperature for 40% of VoriconZole and Ethylene Glycol as shown in Figure. 3.

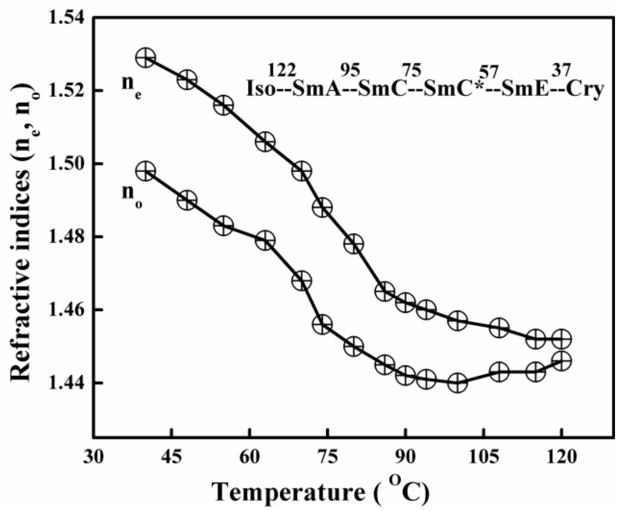


Figure 3. Temperature variations of refractive indices for the mixture of 40% VoriconZole and Ethylene Glycol.

The value of n_e is greater than n_o, indicating that the material is uniaxial positive. From the figure, it can be observed that wherever there is phase transition, the value of refractive indices changes appreciably, which indicates that the changes correspond to polymorphic lyoropic induced chiral smectic modifications. Further, with increase in the concentration of VoriconZole the value of refractive indices decreases with temperature, because the effective optical anisotropy associated with the molecules of

VoriconZole also decreases [24-26].

CONDUCTIVITY MEASUREMENTS

The induced chiral smectic liquid crystalline phase is characterized by molecular self-organization into a phase that has both orientational and positional order; the positional order takes the form of a periodic density wave that is parallel to the average direction of the molecular long axes. In terms of applications: chiral liquid crystalline materials may be used in phenomena such as the electrically addressed bistable display and laser induced optical data storage. The chiral liquid crystalline materials are of very interest: since the SmA phase is stabilized to a high degree of molecular order as compared to non chiral based liquid crystals. The strong tendency towards micro phase separation of each of this mixture stabilizes and promotes the SmA mesophase, leading to wide temperature phase ranges, with properties, such as layer spacing, that are largely temperature independent [27-32] .

Here in present study: 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 lyotropic, thermotropic and also chromonic systems [33]. The temperature variations of electrical-conductivity are as shown in Figure 4,

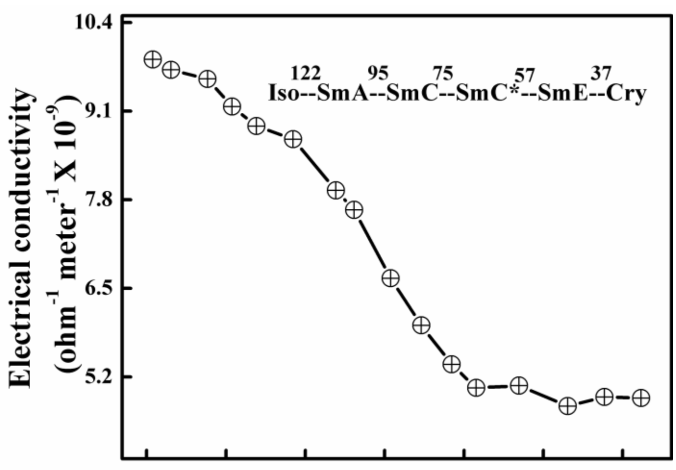


Figure 4. Temperature variation of electrical-conductivity σ (x 10^{-9} Ω^{-1} m^{-1}) for the mixture of 40 % of VoriconZole and Ethylene Glycol.

which clearly illustrates that there is change in the value of electrical conductivity from 40 ^{0}C to 120 ^{0}C, while cooling from isotropic phase for the mixture of 40% VoriconZole and Ethylene Glycol. Mixture of 40% Voriconzole and Ethylene Glycol the phases change from SmA→SmC, SmC→SmC*, SmC*→SmE and SmE→Cryst phases, here if there is some value of electrical conductivity goes on increasing with decreasing the temperature. Changes in electrical conductivity are observed only after further cooling the specimen. This suggests that, the size of aggregates starts growing towards decreasing temperature and the system moves towards more orderliness. Finally, below 37 ^{0}C size of the aggregates becomes so large that the specimen starts moving towards crystalline nature [34, 35].

X-RAY STUDIES

The XRD studies on the liquid crystalline materials were carried out to confirm the phases existing in them, which as suggested by DSC and optical texture studies as well as to study and identify the structural properties of the phase**.** The X-ray diffractometer traces obtained for the mixture of 40% of VoriconZole and Ethylene Glycol at temperature 45 ^{0}C is shown in Figure 5.

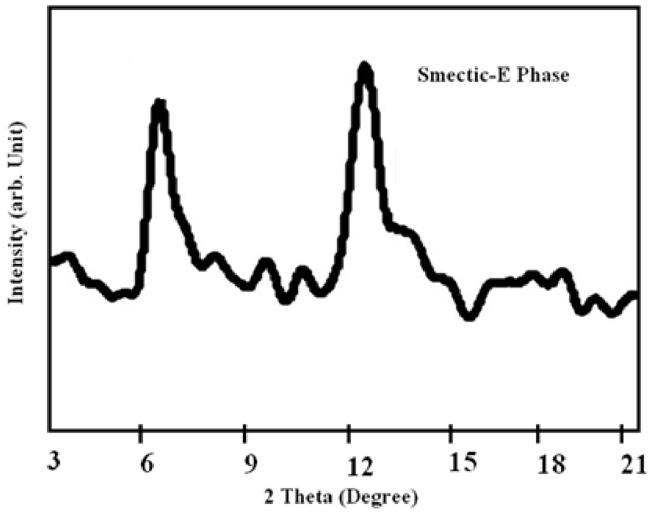


Figure 5. X-ray broadening spectrum for the mixture of 40 % of VoriconZole and Ethylene Glycol at temperature 45 ^{0}C of Smectic-E phase.

The diffraction peaks at this temperature corresponds to Smectic-E phases respectively by using JEOL diffractometer. The x-rays used had a wavelength of 1.54066Å.

In the present project work, X-ray diffraction study is an important method to determine the nano-aggregated grain size of the molecules for different liquid crystalline phases [36, 37]. The deviation from perfect liquid crystallinity leads to 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 Scherrer's formula

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

where L is the nano -aggregated grain size, λ is the wave length of X-ray, K is usually taken as 0.89, β is the line width at half maximum and θ is the diffraction angle. Usually with decrease of temperature [38, 39], the nano-aggregated grain size of the molecules increases. Temperature dependent molecular orientations of focal conic fan texture with radial striation on the fans of focal conic fan texture of smectic-E phase is more stable and hence the molecular ordering of this phase shows two peaks at temperature 45 ^{0}C. The nano-aggregated grain size of liquid crystalline material for smectic-E phase for 40% of given mixtures are comes out to be 48.65 nm. From the X-ray studies, we have been observed that, molecular ordering of the liquid crystalline phase increases with decreasing temperature. X-ray studies clearly illustrate that the nano-aggregated grain sizes are big enough to indicate that the molecular ordering [40-42] of layer structure increases as well as decrease the temperature.

CONCLUSIONS

In light of the above results, we have drawn the following conclusions. The binary mixture of non mesogenic compounds shows the existence of Iso→ SmA→SmC→SmC*→SmE phases for 10% to 70% concentrations of VoriconZole and Ethylene Glycol. Mixtures with the concentrations ranging from 5% to 10% and 70% to 90% of given mixture exhibit only Smectic-A, Smectic-C and Smectic-E phases, sequentially when the specimen is cooled from its isotropic melt. The phase behavior is discussed with the help of phase diagram. The drastic changes in the values of optical anisotropic measurements with variation of temperature unambiguously correspond to polymorphic lyotropic induced chiral smectic phases respectively at different concentrations. X-ray studies are very useful to estimate the grain size of the given molecules at different concentrations of the SmE phase respectively at temperature 45°C. The electrical conductivity studies have also been discussed.

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