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Nano-molecular self assembly and thermal stability of induced mesomorphism in a ternary mixture of liquid crystalline materials

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ABSTRACT

In the present work, our investigation is carried out to study on the optical, thermal and chemical properties of multi-component system of Mefenamic acid (MA), Ethanol+Poly Ethylene Glycol (E+PEG). Mixtures of these molecules exhibit a Smectic-A, Smectic-C, Smectic-E and Smectic-B phases sequentially when the specimen cooled from its isotropic phase. These phases have been characterized by using microscopic technique. The temperature variations of optical anisotropy and X-ray studies have been discussed.

KEYWORDS

Molecular orientation;
Optical textures;
Optical anisotropy.

INTRODUCTION

Liquid crystals are states of condensed matter whose symmetries lie between those of three-dimensionally periodic crystals and isotropic liquids[1-3]. Thermotropic/lyotropic liquid crystalline phases are exhibited by a large number of organic compounds whose molecules have anisotropy of shape. A typical intermolecular energy responsible for the stability of the relevant order in the medium is comparable to the thermal energy and thus liquid crystals are soft materials[4-6].

In our present work, our aim is carried out to study the different properties of three molecules namely, Mefenamic acid (MA), Ethanol+Poly Ethylene Glycol (E+PEG). The mixture of these molecules exhibits a liquid crystalline Smectic-A, Smectic-C, Smectic-E and Smectic-B phases, sequentially when the specimen is cooled from its isotropic phase. These phases have been observed by using microscopic technique and also 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.

EXPERIMENTAL STUDIES

Mixtures of different concentrations of MA+(E+PEG) were prepared and were mixed thoroughly. These mixtures of various concentrations of MA+(E+PEG) 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[7-9].

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. This clearly illustrates that: the mixtures with concentrations ranging from 5% to 90% of MA+ (Ethonal+PEG) exhibit Smectic-A, Smectic-C, Smectic-E and Smectic-B phases and concentrations ranging from 20% to 90% of the mixture shows an Smectic-C phase, sequentially when the specimen is cooled from its isotropic melt. The mixture with concentrations ranging from 5% to 65% of given mixture shows a highly ordered Smectic-B phase respectively at different temperatures. The phase behaviour is discussed with the help of phase diagram[10-12].

Optical texture studies

The polymorphic smectic modifications and the corresponding isotropic to liquid crystalline phase transition temperatures for the mixture with 30% of MA+ (Ethonal+PEG) are given below.

Iso-160 ^{0}C, SmA-145 ^{0}C, Sm C-130 ^{0}C, SmE-102 ^{0}C, SmB-47 ^{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

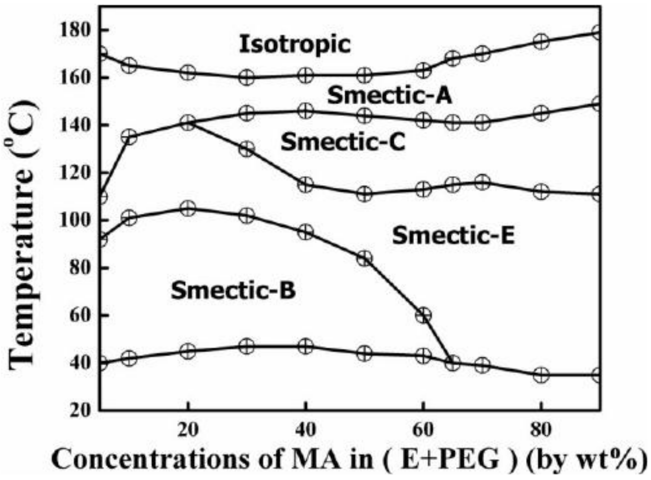
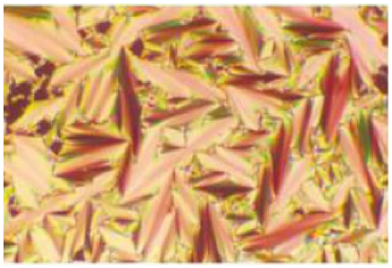
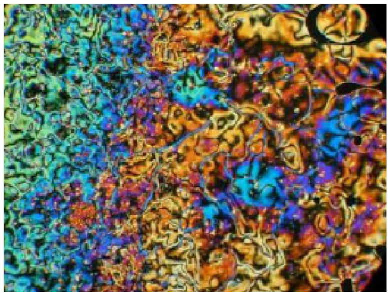


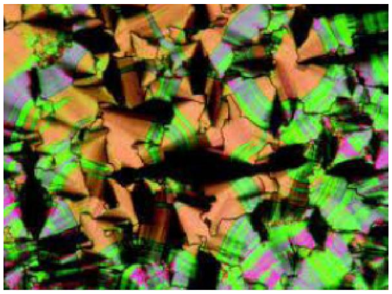
Figure 1 : Partial phase diagram for the mixture of MA+ (Ethonal+PEG)



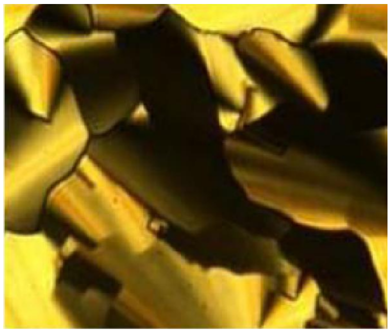
Focal conic fan-shaped texture of SmA phase at temperature 150 ^{0}C (250X



Schlieren texture of SmC phase at temperature 130 ^{0}C (250X)



Focal conic fans with radial striation of smectic-E phase at temperature 112 ^{0}C (250X)



Highly ordered smectic-B phase at temperature 65 ^{0}C (250X)

Figure 2 : Microphotographs obtained in between the crossed polars

appears to be meta-stable, which undergoes slow transformations to give a schlieren texture of smectic-C phase as shown in Figure 2(b). On further cooling, the schlieren texture of smectic-C phase slowly changes over to radial striation[13, 14] of Smectic-E phase as shown in Figure 2(c). In the same way: on further cooling the specimen, Smectic-E phase slowly changes over to paramorphotic[15] focal conic fan-shaped texture of highly ordered smectic-B phase as shown in Figure 2(d), in which the molecules are arranged in hexagonal close-packed structure. At this transition: phase changes from smectic-E to smectic-B phase and hence it is clearly observed that: there is a drastic change in the values of refractive index and electro-conductivity of the given mixture[16, 17]. This anomalous behavior is presumably associated with the high degree of order of molecular arrangement in smectic-B phase and then it becomes crystalline phase at room temperature. It can be noticed that, the observed phase transition temperatures are different from the values have been observed in a similar type of study by TNG and Nagappa et al.,[18, 19] in which the mixture of a different compound with organic solvents has been studied. Hence, the interaction of organic solvents looks to be different with different compounds.

Optical anisotropic studies

The refractive indices of a liquid crystal are mainly determined by the molecular structure, wavelength and operating temperature. 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[20, 21]. Results of this investigation 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 different concentrations of given mixture by using Abbe Refractometer. Temperature variations of refractive indices for the sample of 30% MA + (Ethonal+PEG) as shown in Figure 3. 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 smectic modifications. Further, with increase in the concentration of mefenamic acid the value of refractive indices decreases with temperature, because the effective optical anisotropy associated with the molecules of mefenamic acid also decreases[24-26].

Ray studies

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.

X-ray diffractometer traces obtained for the mixture of 30% of MA+ (Ethonal+PEG) at temperature 58 ^{0}C is shown in Figure 4. The diffraction peaks at this temperature corresponds to Smectic-B phase respectively by using JEOL diffractometer with the settings: TC4, CPS400, channel width 100 for λ = 1.934 Å). In the present study, X-ray diffraction study is an important method to determine the nano-aggregated grain size of the molecules for different liquid crystalline phases[27, 28]. The deviation from perfect liquid crystallinity leads to broadening of the diffraction peaks. In order to estimate the nano-aggregated grain size of given molecules for different liquid crystalline phases corresponding to broadening of X-ray diffraction peaks we have used the Scherrer's formula

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

where L is the nano -aggregated grain size, λ is the wave length of X-ray radiation (Fe: 1.934 Å), K is

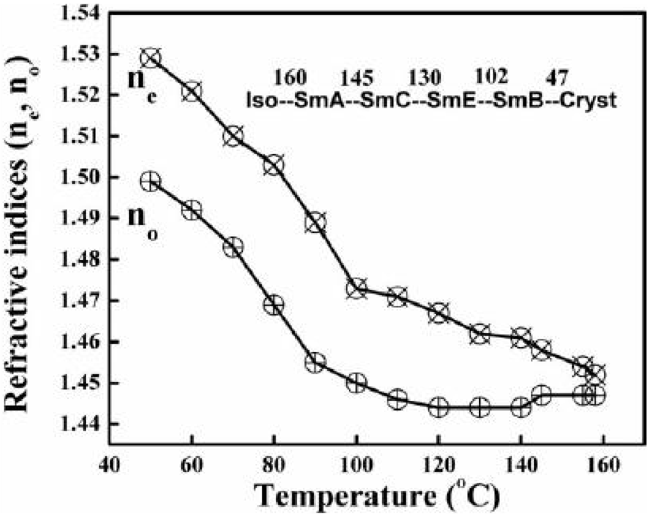


Figure 3 : Temperature variations of refractive indices for the mixture of 30% MA+ (Ethonal+PEG)

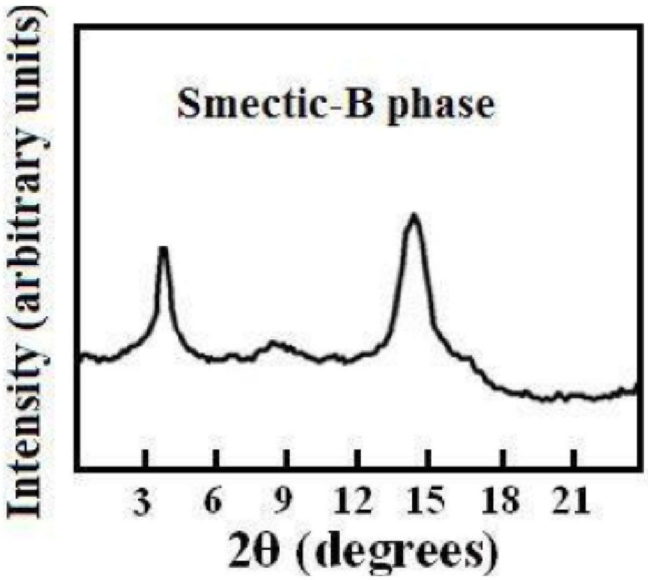


Figure 4 : X-ray broadening spectrum for the mixture of 30% of MA+ (Ethonal+PEG) at temperature 58 ^{0}C of Smectic-B phase

usually taken as 0.89, β is the line width at half maximum and θ is the diffraction angle. Usually with decrease of temperature[29, 30], the nano-aggregated grain size of molecules increases. Temperature dependent molecular orientations of highly ordered smectic-B phase is more stable and hence the molecular ordering of this phase shows two peaks. The nano-aggregated grain size of given mixture for smectic-B phase are comes out to be 28.32 nm. From X-ray studies, we have been observed that, the molecular ordering of liquid crystalline phase increases with decreasing temperature. X-ray studies clearly illustrate that: the nano-aggregated grain sizes of the given molecules are big enough to indicate that, the molecular ordering[31-33] of layer structure increases as well as decrease the temperature.

CONCLUSIONS

In light of the above results, we have drawn the following conclusions. Multi-component system of MA+(Ethonal+PEG) shows the existence of Iso-SmA-SmC-SmE-SmB phases for different concentrations of given mixture. The phase behavior is discussed with the help of phase diagram. Drastic changes in the value of temperature dependent optical anisotropic unambiguously corresponds to polymorphic smectic phases, respectively at different temperatures and at different concentrations.

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