

Anisotropic molecular orientation of opto-electrical and density studies on induced mesomorphism liquid crystalline materials

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ABSTRACT

In the present work, our investigation is carried out to study on the optical- electrical 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-density and ultrasonic measurements and electrical conductivity have been discussed.

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KEYWORDS

Molecular orientation;
Optical textures;
Optical anisotropy.

INTRODUCTION

Liquid crystals are primarily liquids but also share properties of crystalline materials. Usually, liquids are characterized by isotropic macroscopic properties and by the ability to flow while crystals are characterized by long range positional order which leads to anisotropic macroscopic properties. Like liquids, liquid crystals exhibit fluidity. They are made up of organic molecules characterized by anisotropic molecular properties and by short range molecular interactions which couple over many molecular diameters to produce long range orientational order^[1, 2]. These characteristics results are in anisotropic macroscopic properties such as birefringence, density, susceptibilities and optical studies etc.

In the present investigation, our aim is to carry out the study of different properties of multi-component system of liquid crystalline materials^[3, 4]. All

concentrations of given mixtures exhibits a induced polymorphism of different smectic phases sequentially when they are cooled from its isotropic melt. The temperature variations of optical anisotropy and electrical conductivity have been discussed.

EXPERIMENTAL STUDIES

Mixtures of different concentrations of MA in (E+PEG) were prepared and were mixed thoroughly. These mixtures of various concentrations of MA in (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 micro-

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scopic observations. A capillary Pycnometer with a diameter of about 0.2 mm was used for density measurements. The permitted temperature control was $\pm 0.1^\circ\text{C}$. The level of liquid crystal in the capillary was read to $\pm 0.01\text{mm}$ with a cathetometer. The absolute error in the density measurements was $\Delta\rho = \pm 0.0001\text{ g/cc}$. Electrical-conductivity measurements of the mixture at different temperatures were carried out using digital LCR meter and a proportional temperature control unit. IR spectra at 299 K were recorded using a Perkin–Elmer IR spectrometer to understand the layer structure and intermolecular interaction.

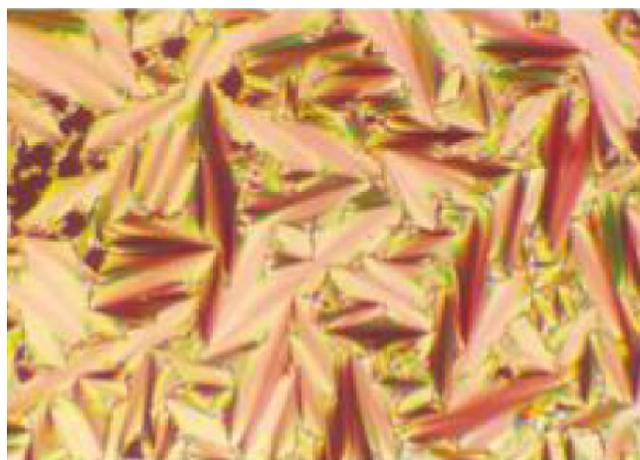
RESULTS AND DISCUSSIONS

Optical texture studies

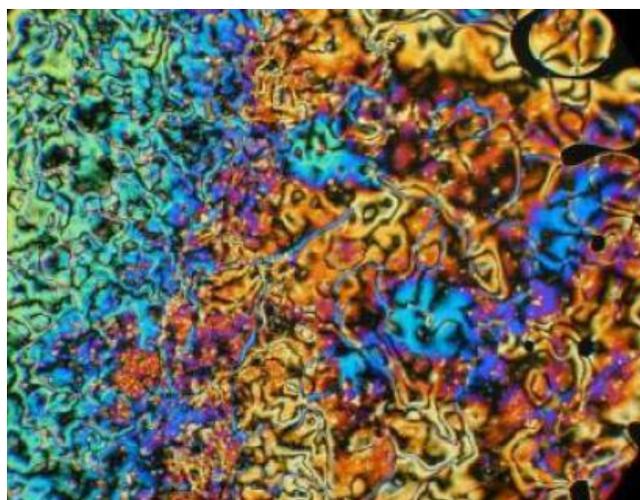
The polymorphic smectic modifications and the corresponding isotropic to liquid crystalline phase transition temperatures for the mixture with 30% of MA+ (E+PEG) are given below.

Iso-160 °C, SmA-145 °C, Sm C-130 °C, SmE-102 °C, SmB-47 °C.

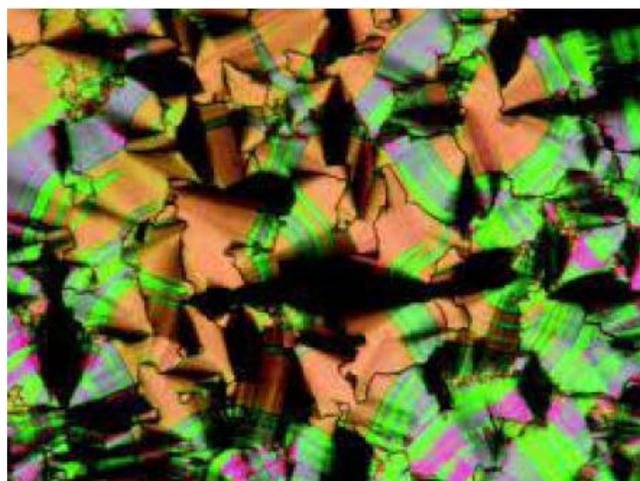
On cooling the specimen from its isotropic melt, the setting point is marked by the genesis of nucleation at several points which appear as minute bubbles initially, but which progressively grow radially and form a focal conic fan texture of smectic-A phase in which the molecules are arranged in layers and the texture is shown in Figure 1(a). This phase appears to be meta-stable, which undergoes slow transformations to give a schlieren texture of smectic-C phase as shown in Figure 1(b). On further cooling, the schlieren texture of smectic-C phase slowly changes over to radial striation^[5, 6] of smectic-E phase as shown in Figure 1(c). In the same way: on further cooling the specimen, smectic-E phase slowly changes over to paramorphic^[7] focal conic fan-shaped texture of highly ordered smectic-B phase, 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^[8, 9]. This anomalous behavior is presumably associated with the high degree of order of molecular arrangement



Focal conic fan-shaped texture of SmA phase at temperature 150 °C.



Schlieren texture of SmC phase at temperature 130 °C.



Focal conic fans with radial striation of smectic-E phase at temperature 112 °C.

Figure 1 : Microphotographs obtained in between the crossed polars

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.,^[10, 11] 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.

Density measurement

Temperature variations of density for the sample of 40% MA in (E+PEG) as shown in the Figure 2, which clearly illustrates that: the density increases linearly with decrease of temperature in the optical region between isotropic and crystalline phase of given mixture. The phase transition is very nearer to isotropic and smectic-A region, in this transition at particular region a sudden jump has been observed in the values of density. A sudden jump in the value of density shows the increases its value hence it indicates that: the phase transition region in between isotropic and smectic-A phase transition is probably first order. A sudden jump in the value of density at optical region is attributed to a sudden change in the molecular structure, that they were confirmed macroscopically by microscopic technique. The higher values of density in the smectic-A phase region are more than that of in isotropic region: which clearly indicates that, the tendency of increasing molecular order is more with decrease of temperature^[12, 13], the pre-transitional effects at optical re-

gion between isotropic and smectic-A phase transitions are found to observed on the lower side of the transition, which supported by Maier-Saupe theory^[14]. After isotropic transition, at smectic-A phase region the density of given mixtures increases linearly with decrease of temperature and then at the optical region between smectic-A and smectic-C phase transition: the values of density show an increasing nature. From the measured of higher value of density of the given mixture and the literature survey of thermal expansion coefficient clearly indicate that: the transition is first order. The measured higher value of density and thermal expansion coefficient indicate that: the phase transition is first order. Our measurements are in accordance with Torza and Cladis on CBOOA. Densities of the given mixtures are increases gradually with decrease of temperature in smectic-C phase. The increasing values of densities: that has been experimentally observed at different optical regions with decrease of temperature towards the crystalline phase. The structural confirmations of molecular density of different liquid crystalline phases such as smectic-A–smectic-C–smectic-E–smectic-B phases have been macroscopically observed by microscopic technique at different concentrations and at different temperature. The measurements of increasing values of densities across at different optical regions are more predominant than one to other optical regions.

Conductivity measurements

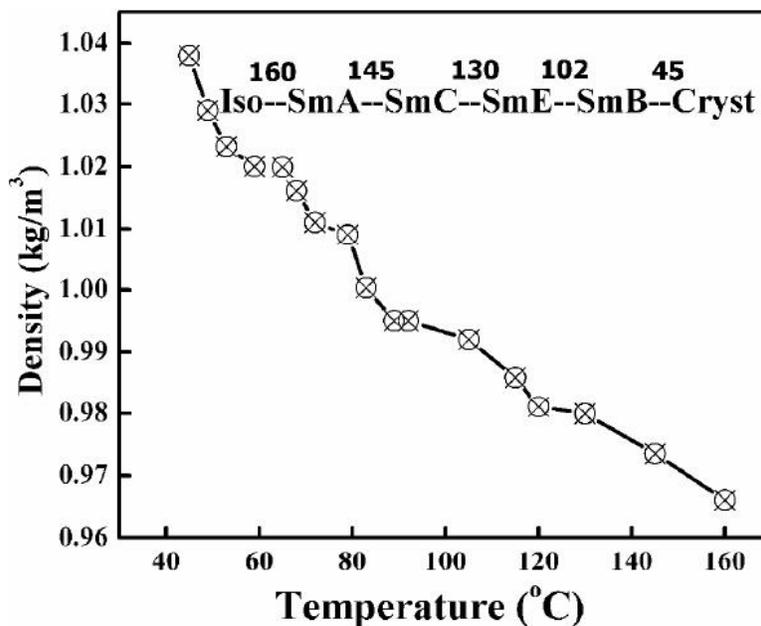


Figure 2 : Temperature variations of density for the sample of 40% MA in (E+PEG)

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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^[15]. The temperature variations of electrical conductivity are shown in Figure 3, which clearly illustrates that there is some change in the value of electrical conductivity from 50 °C to 155 °C, while cooling from isotropic phase for the mixture of 40% of MA+(E+PEG). Mixture of 30% MA+ (E+PEG), the sequence of phases have been changes from Iso-SmA-SmC-SmE-SmB phases respectively at different temperatures. Here it has been found that: the electrical conductivity goes on increasing as the temperature decreases. This suggests that aggregated molecular size starts growing towards lower temperatures and then the system becomes more ordered^[16-22].

IR studies

In this study, prodrugs of mefenamic acid serve as building blocks of the unit. In this unit, if we have been observed how atoms are connected together, which bonds are single, double, or triple and we can explain what functional groups exist in the given molecules. From the fundamental IR spectroscopic display, we have been observed two regions such as group frequency region (4000-1250 cm^{-1}) and finger print region (1250-400 cm^{-1}). In the group fre-

quency region absorption bands are characteristic of specific groups of atoms and relatively independent of composition of the rest of the molecule. In Group Frequency region, the vibrational frequency of a given functional group can be pin pointed to a much narrower range of frequencies. The group frequency region is extremely useful for diagnosing the presence or absence of certain functional groups. In finger print region, the vibrational frequencies are profoundly affected by the molecular structure as a whole. Therefore bands in this region are considered specific for a particular molecule rather than for a particular functional group. From the IR spectrum we extract the information's of IR spectral data (OH -3433, NH-3311, C=O-1649), which indicated the standard pro-drug of mefenamic acid had COOH groups. The structures of PEG 1500/6000-mefenamic acid (OH -3433, 2° NH-3311, C-O-C-1149, CH str-2886, C=O-1649) were confirmed by IR. From this observation which we confirm that carboxyli group of mefenamic acid formed an ester; the structures are as shown in scheme I and it is presented in Figure 4. The Figure 5 shows IR spectra for the mixture of MA+(E+PEG). From the Figure 5, the attached group of mefenamic acid, PEG and ethanol were confirmed by IR spectra and hence it is observed that functional group can be pin pointed^[23] to a much narrower range of frequencies 1649.92 cm^{-1} . We are concluded the expected functional group (C=O) esters are present in our prod-

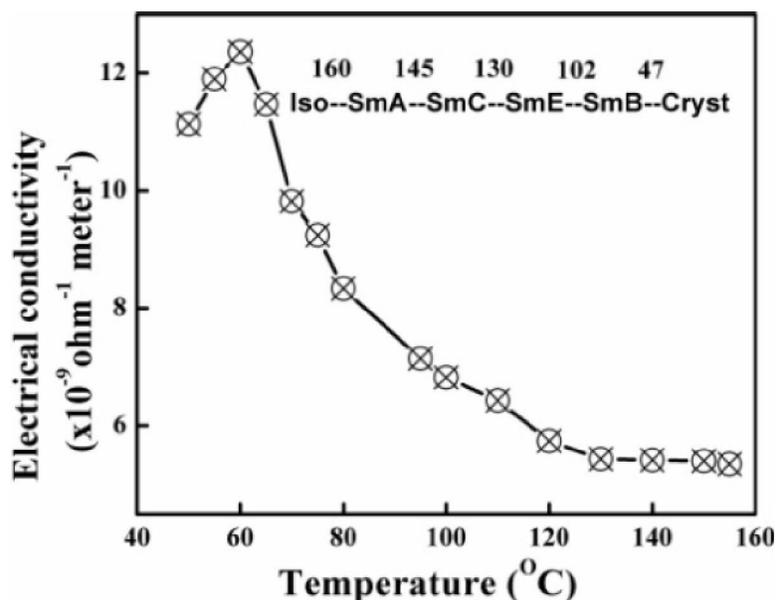


Figure 3 : Temperature variation of electrical-conductivity σ ($\times 10^{-9} \text{ \&!}^{-1} \text{ m}^{-1}$) for the sample of 40% of MA+ (E+PEG)

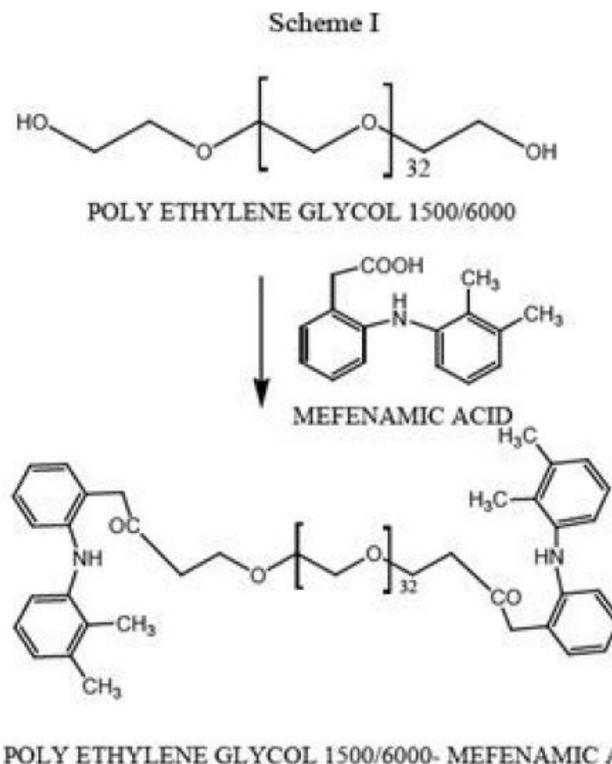


Figure 4 : The molecular attachment of sheet like structure for the sample of MA+ (E+PEG)

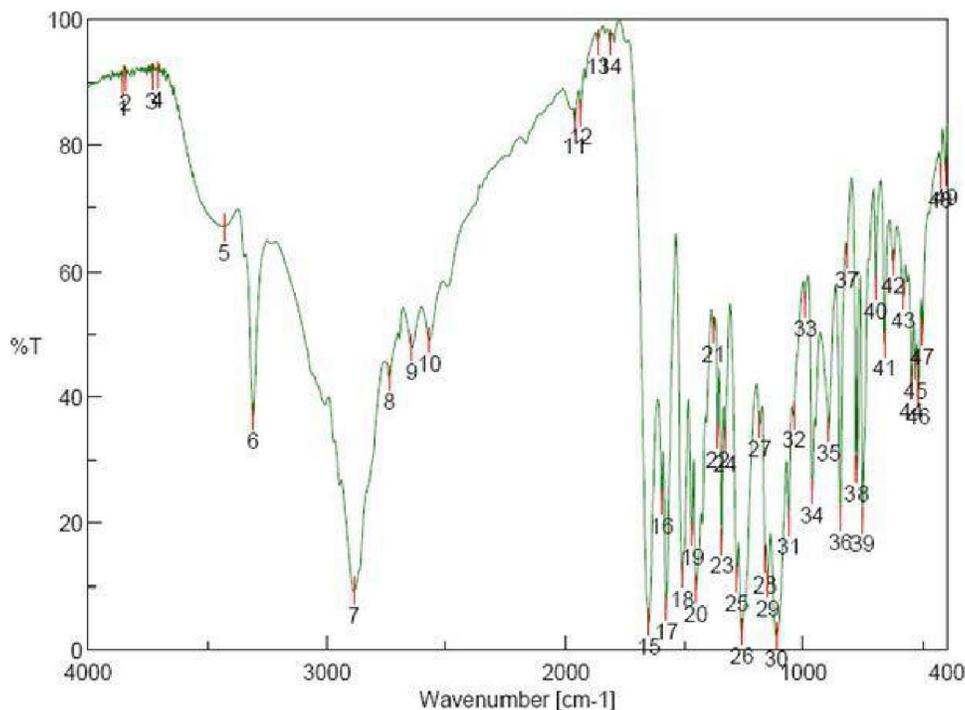


Figure 5 : IR spectra obtained for the mixture of MA+ (E+PEG)

uct. This clearly shows that mefenamic acid is associated with ethanol and polyethylene glycol helps to form the lyotropic smectic phases. Lyotropic mesophases are characterized by lamellar, hexagonal and cubic structures. In lamellar domain most of the defects are spherulitic or batonnets where the

molecular packing with spherical bilayers in the form of onions. The Friedels oily streaks^[24-26] are also observed. Occasionally the mixtures of higher concentrations of amphiphilic compounds exhibit classic focal conic domains, which are characterized by a fan shaped texture.

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 changes in value of electrical conductivity with the variation of temperature unambiguously correspond to induced polymorphic smectic phases. Drastic changes in electrical conductivity are expected to be due to changes in the dimension of disks along with changes in the orientation order of the arrangement. From the IR studies: the arrangement of attached molecules in the present mixture clearly shows how the carboxyl groups are present and hence to form esters in given mixture. This studies helps us to understand the molecular orientations of given molecules shows the existence of lamellar, hexagonal and cubic liquid crystalline phases.

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