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OPTICAL ANISOTROPIC PHASE TRANSITION STUDIES ON MESOMORPHIC PROPERTIES OF TERNARY MIXTURES OF MEFENAMIC ACID, ETHANOL AND POLY ETHYLENE GLYCOL

Physics

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KEYWORDS

Phase transition; Molecular orientation; layer spacing's; Tilt angle, IR studies.

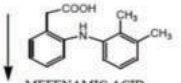
INTRODUCTION

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. Relatively weak interactions like those between molecular dipoles or chiral centers of appropriate molecules can give rise to new types of liquid crystals. The soft nature of the medium, coupled with anisotropic optical and dielectric properties gives rise to many electro-optic effects at relatively low voltages. These are exploited in liquid crystal displays, which are the lowest power consuming flat panel devices and used in all calculators, laptop and palmtop computers, cell phones, full-size television screens, etc. [4-6].

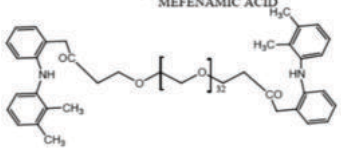
In our present project work, our aim is to study the mixture of multi-component system, namely, Mefenamic acid (MA), Ethanol+ Poly ethylene glycol (E+PEG), which exhibits liquid crystalline Smectic-A, Smectic-C, Smectic-E and Smectic-B phases, sequentially when the specimen is cooled from its isotropic liquid phase. These phases were observed 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. From the IR studies Mefenamic acid serves as building blocks of the unit. In this unit, Ethanol and Poly ethylene glycol molecules are attached to the COOH molecule, which is as shown in Figure.1

Scheme I

POLY ETHYLENE GLYCOL 1500/6000



MEFENAMIC ACID



POLY ETHYLENE GLYCOL 1500/6000- MEFENAMIC ACID

Experimental Studies

In the present work we have been considered the compounds namely, Mefenamic acid (MA), Ethanol+ Poly ethylene glycol (E+PEG) 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 MA+(Ethonal+PEG) were prepared and were mixed thoroughly. These mixtures of various concentrations of MA+ (Ethonal+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 Meopta Polarizing Microscope (POM) with hot stage and camera attachment was used to record the textures of the samples. Canon EOS Digital REBEL XS/ EOS1000D is a digital single lens reflex camera is used to record the texture images of the samples through the crossed polarizer's of the POM. The X-ray diffraction patterns were obtained using SHIMADZU -XRD-6000 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

Studies On The Structural Stability Of Partial 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 2. This clearly illustrates that mixtures with the concentrations ranging from 5% to 90% of MA+(Ethonal+PEG) exhibit Smectic-A, Smectic-C, Smectic-E and Smectic-B phases, sequentially when the specimen is cooled from its isotropic melt. But the mixtures with concentrations of MA+(Ethonal+PEG) ranging from 20% to 90% of given mixture clearly shows an Smectic-C phase at different temperatures and at different concentrations of the given mixture. The mixture with concentrations ranging from 5% to 65% of MA+ (Ethonal+PEG) shows an Smectic-B phase respectively at different temperatures. The phase diagram clearly shows polymorphic smectic phases such as Smectic-A, Smectic-C, Smectic-E and Smectic-B phases [10-12].

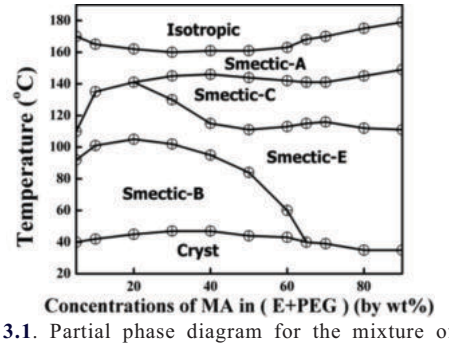


Figure 3.1. Partial phase diagram for the mixture of MA+ (Ethonal+PEG).

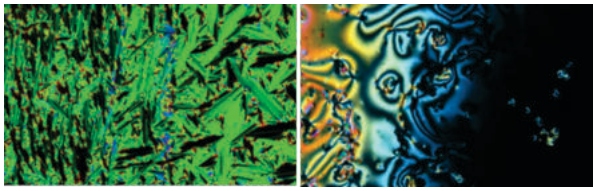
Studies On Mesomorphic Properties Of Liquid Crystalline Phases

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.

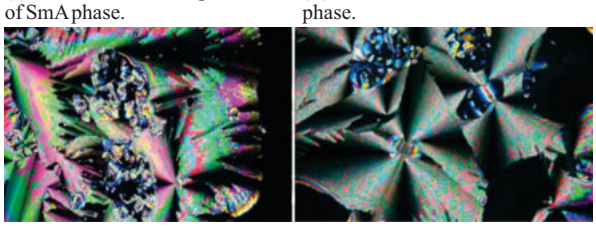
Iso-160 ^{0}C, SmA-145 ^{0}C, SmC-130 ^{0}C, SmE-102 ^{0}C, SmB-47 ^{0}C.

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.3(a). This phase appears to be metastable and undergoes slow transformations to give schlieren texture of smectic-C phase as shown in Figure 3 (b) on cooling the specimen. On further cooling, focal conic fan texture with radial striation on the fans [13,14], which is the characteristics of Smectic-E phase, is observed and it is shown in Figure 3(c). On further cooling the specimen, Smectic-E phase slowly changes over to paramorphotic [15] focal conic fan-shaped texture of ordered smectic-B phase is shown in Figure 3(d) in which the molecules are arranged in hexagonal close-packed structure. At this phase transition, i.e, from smectic-E phase to smectic-B phase, it is observed that there is a drastic change in the values of refractive index and electroconductivity of the sample [16, 17]. This anomalous behavior is presumably associated with high degree of order of the molecular arrangement in smectic-B phase and then it becomes crystalline phase at room temperature. It can be noticed that the phase transition temperatures observed in this study are different from the values 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.



(a) Focal conic fan-shaped texture of SmA phase. (b)Schlieren texture of SmC phase.



(c)Focal conic fans with radial striation of smectic-E phase. (d) Broken banded focal conic fan shaped texture of smectic-B phase.

Figure 3. Microphotographs obtained in between the crossed polars.

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. 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 this paper 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 65%of MA+(Ethonal+PEG) are shown in the following table. From the table: the value of ne is greater than no, 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]. Table 1: The variations of refractive indices as a function of temperature for 65%of MA+(Ethonal+PEG).

Temp (^oC)	45	52	59	63	69	75	80	86	95	102	110	118
n_e (e-ray)	1.4269	1.4258	1.4246	1.4232	1.4218	1.4213	1.42	1.419	1.4187	1.4183	1.418	1.4179
n_o (o-ray)	1.4223	1.4211	1.4192	1.4181	1.4172	1.4166	1.4164	1.4164	1.4168	1.417	1.417	1.4171

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 65% of MA+ (Ethonal+PEG) at temperature 58 ^{0}C is shown in Figure 4. 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 work, 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 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 [29, 30], the nano-aggregated grain size of the molecules increases. Temperature dependent molecular orientations of stirration of smectic-E phase is more stable and hence the molecular ordering of given phase shows three peaks. The nano-aggregated grain size of liquid crystalline materials for smectic-E phase are comes out to be 39.63 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 [31-33] of layer structure increases as well as decrease the temperature.

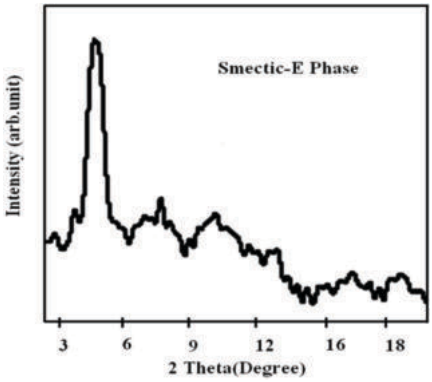


Figure 4.X-ray broadening spectrum for the mixture of 65% MA+ (Ethonal+PEG) at temperature 58 ^{0}C of Smectic-E phase.

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 funadamental IR spectroscopic display, we have been observed two regions such as group frequency region (4000-1250cm^{-1}) and finger print region (1250-400cm^{-1}). In the group frequency 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 the finger print region, 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 it contains the information's of IR spectral data (OH -3433, NH-3311, C=O-1149), which indicated that standard pro-drug of mefanamic acid had a COOH group by IR. The structures of PEG 1500/6000-mefenamic acid (OH -3433, 2° NH-3311, C-O-C-1149, CH str-2886, C=O-1149) were confirmed by an IR and COOH group of mefenamic acid had formed an ester; the structures were observed the given standard scheme which represent the IR spectra of standard drug mefenamic acid and IR spectra of PEG 1500/6000-mefenamic acid. Fromm this studies 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 [38] to a much narrower range of frequencies 2886.92 cm^{-1} . We are concluded expected functional group (H-C=O: C-H) aldehydes are present in our product [34]. This clearly shows that mefenamic acid is associated with ethanol and polyethylene glycol helps to form the smectic phases.

CONCLUSIONS

In light of the above results, we have drawn the following conclusions. The multi-component system of MA+ (Ethonal+PEG) shows the existence of Iso→ SmA→SmC→SmE→Sm**B** phases for all

concentrations of given mixture. The phase behavior is discussed with the help of phase diagram. The drastic changes in the optical anisotropic measurements with variation of temperature unambiguously correspond to polymorphic smectic phases, respectively at different concentrations. The arrangements of attached molecules in the present mixture show how the COOH groups are present to form esters in the given mixture. It has been confirmed from IR studies, expected functional groups are aldehydes, which are present in our product and it helps to form a different liquid crystalline phases in present case.

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