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Dielectric studies and nano-molecular self assembly of lyotropic chromonic liquid crystalline phases

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ABSTRACT

In the present work, our investigation is to study the optical and dielectric properties of the binary mixture of Abietic acid in Ethylene glycol which exhibits a very interesting liquid crystalline biphasic region of aggregated columnar (C+I) and columnar (C) phases sequentially when the specimen cooled from isotropic phase. These phases have been characterized by using microscopic and optical anisotropic technique. The temperature variations of dielectric parameters have also been discussed. X-ray studies are supported to calculate the nano-aggregated grain size of the molecules.

KEYWORDS

Phase transition;
Molecular aggregation;
Optical anisotropy;
Dielectrics.

INTRODUCTION

In recent years, the existence of a second class of aqueous lyotropic mesophases, termed chromonic liquid crystals, has come to be better recognized and understood[1,2]. Unlike typical lyotropic phases formed by amphiphilic molecules having a hydrophilic head and a hydrophobic tail, chromonic liquid crystals are formed by water-soluble molecules that contain planar aromatic rings. Examples of chromonic liquid crystal-forming molecules include drugs, dyes, and nucleic acids[3].

Some of the researches have been found to study the molecular dynamics of drugs, dyes, nucleic acids and solvent systems; they have to focus exclusively on the isotropic to smectic[3-8] phase transitions as a function of solvent type and concentration. Temperature dependent molecular kinematic tend to aggregate into stacks due to both weak Vander Waals interactions between the cores and the hydrophobic effect. At all concentrations, there is some degree of aggregation. As the concentration increases, the distribution of aggregate size shifts to higher and higher numbers of molecules in the aggregates.

The dielectric and optical studies provides useful information about the molecular structure, dynamics, phase transition and display performance of liquid crystals, but the dielectric studies on smectic phases have been performed less than nematics and ferroelectric liquid crystals[4-8]. Similarly from application point of view the knowledge of optical anisotropy and refractive indices of liquid crystals and their temperature dependence is also of much importance[9, 10].

In the present investigation, we have carried out to show the existence of co-existent biphasic region of aggregated columnar (C+I) and columnar (C) phases

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sequentially when they are cooled from its isotropic phase. Optical texture studies have been carried out for the molecular aggregation of the phases at different temperatures. In light of the investigations, an attempt has been made to understand the coupling between aggregate structure and the mesophase order in light of the observations regarding lyotropic, chromonic liquid crystals[4], where-in it has been observed that, the aggregates formed for all concentrations of the given mixture are large enough to align, and there by aggregate size increases into supramolecular assemblies.

EXPERIMENTAL SECTION

In the present investigation, we have studied binary mixtures of liquid crystalline materials, namely, Abietic acid 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. Ethylene glycol was supplied from Kodak, Ltd., Kodak house, Mumbai, India. The structural formulae for Abietic acid and ethylene glycol molecules are as shown in Figure 1(a, b). Concentrations of 65% Abietic acid in Ethylene glycol have been considered for the experimental studies and it was 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 temperature of this concentration was measured with the help of Leitz-polarizing microscope in conjunction with 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 at different temperatures using JEOL diffractometer. Electrical-conductivity measurements of the mixture at different temperatures were carried out using digital LCR meter and a proportional temperature control unit[11].

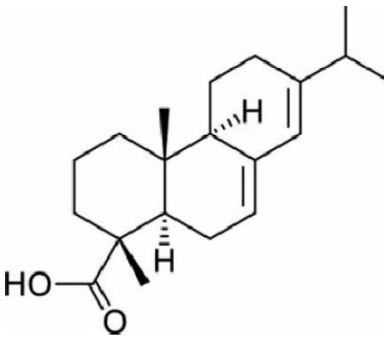

Figure 1(a) : The structural formula for Abietic acid

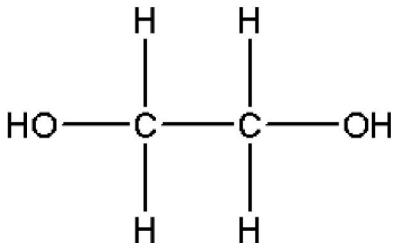

Figure 1(b) : The structural formula for ethylene glycol molecules

MEASUREMENT OF DIELECTRIC STUDIES

The values of capacitance and dissipation factor of the sample holder with, and without sample, were determined by impedance / gain phase analyzer of Hewlett-Packard (HP 4194A). The real part of the permittivity of the sample is obtained from the change in the capacitance value of the sample holder, due to the presence of sample, using the following equation:

$$\epsilon' = \frac{\Delta C}{C_G} + 1$$

where, ΔC, the change in the capacitance of sample holder due to the presence of sample, is

$$\Delta C = C_P - C_O$$

where, C_P is the capacitance with sample, and C_O is the capacitance without sample. C_G is the geometrical capacitance of the sample holder.

The loss tangent and dissipation factor (D) of the sample were derived from the dissipation factor and capacitance, measured for the sample holder with, and without sample, and is given by:

$$\tan\delta = \frac{C_P D_P - C_O D_O}{C_P - C_O}$$

where, D_P is the dissipation with sample, and D_O is the dissipation without sample.

The loss factor is given by the following equation

$$\epsilon'' = \epsilon' \tan\delta$$

The values of capacitance and dissipation factor were recorded. The temperature of the sample was maintained by placing the sample cell on a specially designed double walled brass chamber, in

which heated oil was circulating, with the help of a Julabo F-25 refrigerated circulator. It has the facility of setting the temperature of the sensor used, and so the temperature of the sample, i.e. the sensor temperature, has been measured directly from the display of the monitor (Operating Manual, JULABO). The temperature was measured by placing a thermocouple in close vicinity to the sample, with an accuracy of 0.1^0C.

RESULTS AND DISCUSSION

Optical texture studies

In the present study, optical textures exhibited by the samples were observed and recorded using Leitz polarizing microscope and constructed hot stage. The specimen was taken in the form of thin film and sandwiched between slide and cover glass. Concentrations of 65% Abietic acid in Ethylene glycol have been considered for the experimental studies. 65% of the given mixture slowly cooled from its isotropic melt. A genesis of nucleation starts in the form of molecular orientations, which is growing and segregates the molecules, which are identified as the co-existent biphasic region of aggregated columnar (C+I) phase. On further cooling, C+I phase changes over to columnar (C) phase and then this phase remains stable up to room temperature.

For most of the phase diagrams, the biphasic region of aggregated columnar (C+I) phase is found to be unstable. However, when aggregation is very weak (high temperature), the columnar + isotropic (C+I) phase becomes unstable with respect to a liquid crystalline isotropic phase. In addition to the macroscopic phase behavior, our calculations also give detailed information on the microscopic state of the self assembled system. These include average aggregated size, orientational order parameter and inter columnar spacing in the columnar phase. As expected, the average aggregate size increases monotonically with increasing concentrations as well as with decreasing temperature[12].

Dielectric parameters

The dielectric studies are very useful information about molecular structure, molecular dynamics and phase transition behavior and they are used as an input to its display applications[13, 14]. In addition; the dielectric anisotropy and dielectric loss of the liquid crystal arising from angular correlation between the molecules, not only throw light on individual molecular structure but also their ordering in a particular mesophases, which may be characterized by order parameter. Since the value of dielectric permittivity and dielectric loss vary with the variation of temperature, these parameters can be used to measure the transition temperatures of pure liquid crystals as well as their mixtures.

At constant frequency 5 kHz, the temperature variations of dielectric parameters such as dielectric constant (ε') and dielectric loss (ϵ'') have been measured for the mixture of 65% Abietic acid in Ethylene glycol is presented in Figure 2(a-b). From the figure it is clear that, the discontinuities are observed; while the phase transition temperature changes the different liquid crystalline phases, which are appear from crystalline - isotropic region. The dielectric parameter ϵ' decreases with increasing the temperatures and the parameter ϵ'' increases with increasing the temperatures and hence the most remarkable feature of these parameters are more tendency to their constituent molecules are segregate in space with the creation of interfaces, which is due to the fact that, the domination of interfacial polarization over dipole polarization. Therefore, it can be concluded that, the interfacial polarization is responsible for the dielectric relaxation of the molecules. The

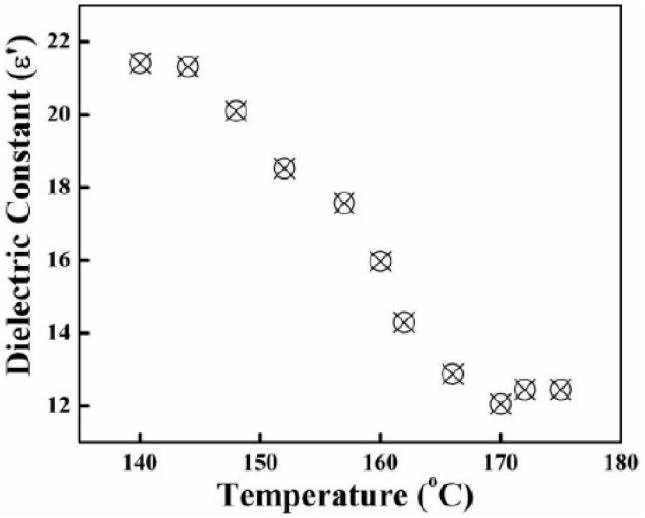

Figure 2(a) : Temperature variation of dielectric constant for the given sample

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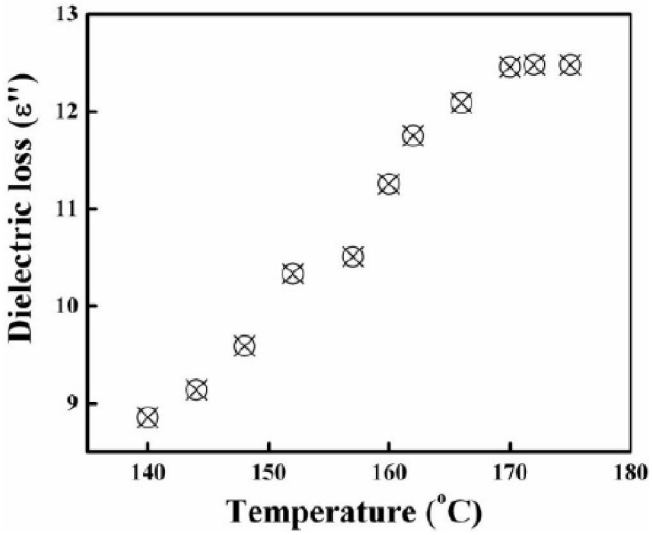

Figure 2(b) : Temperature variation of dielectric loss for the given sample

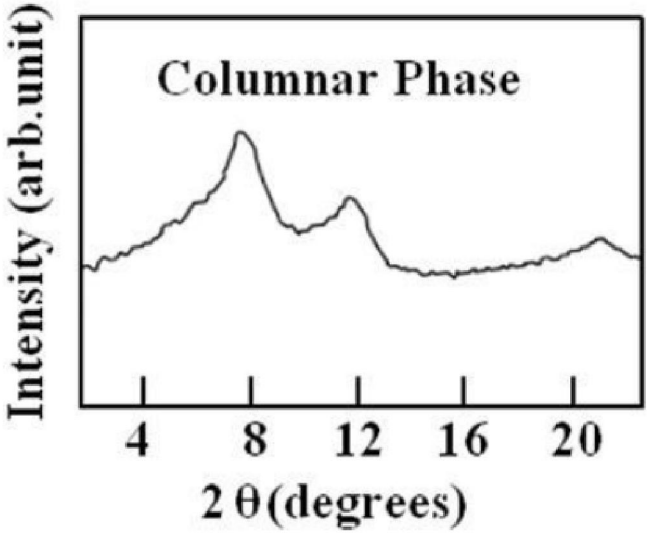

Figure 3 : X-ray broadening spectrum for the given sample at 60 ^{0}C temperature of columnar phase

phase transition from crystalline- isotropic region, the molecular twist can be of different liquid crystalline phases, which shows different molecular orientational directions in between these regions. Hence the change in dielectric parameters are remains uniform, when it appears nearer to isotropic region, for both parallel and perpendicular orientations and they giving rise to an overall positive dielectric anisotropy caused by the considerable longitudinal dipole moment. This may lead to the conclusion that the dipole moment exhibits anti-parallel correlations in the isotropic phase of the given molecules[15-25].

Characterization of nano aggregated grains

The X-ray diffractometer traces obtained for the mixture of 65% Abietic acid in Ethylene glycol at temperature 60 ^{0}C is shown in Figure 3. The diffraction peaks at this temperature correspond to columnar phase respectively by using JEOL diffractometer with the settings: TC4, CPS400, channel width 100 for λ = 1.934 Å). X-ray diffraction study is an important method to determine nano-aggregated grain size of the molecules for different liquid crystalline phases[26, 27]. 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 radiation (Fe: 1.934 Å), 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[28, 29], nano-aggregated grain size of the molecules increases. A temperature dependent molecular orientation of columnar phase is more stable and hence the molecular ordering of this phase shows two peaks. The nano- aggregated grain size of liquid crystalline material for columnar phase comes out to be 43.59 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[30-32] of layer structure increases as well as decrease the temperature.

CONCLUSIONS

In light of the above results, we have drawn the following conclusions. The given binary system exhibits an unusual sequence of phases showing the formation of a co-existent biphasic region of aggregated columnar (C+I) and columnar (C) phases respectively at different temperatures. Changes in the values of dielectric parameters shows the molecules are segregate

in space with the creation of interfaces, which is the domination of interfacial polarization over dipole polarization. The changes in dielectric parameters are same in isotropic region, which shows positive dielectric anisotropy caused by the considerable longitudinal dipole moment. This may lead to the conclusion that the dipole moment exhibits anti-parallel correlations in the isotropic phase of the given molecules. The X-ray study lends support to found nano-aggregated size of for columnar (c) phase comes out to be 43.59 nm.

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