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Optical Anisotropy of Space Charge and Activation Energy Studies on Cholesteric to Smectic Phases

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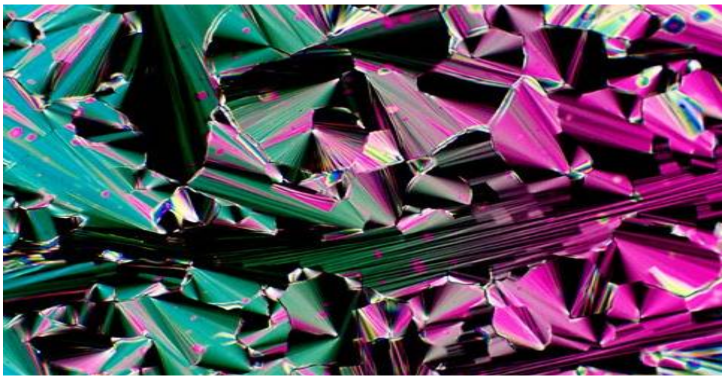
ABSTRACT

Optical phase transition studies on binary mixtures of cholesterol isobutyl corbonate (CIB) and 4-(trans-4'-hexylcyclohexyl) isothiocyanatobenzenes (6CHBT) molecules exhibits spherulitic texture of cholestric and induced chiral smectic phases. Mixtures of different concentrations of cholesteric material in accordance to the sequence: when the temperature of the molecules in its isotropic phase is brought down to a cooler temperature. The space charge relaxation time and activation energy of given molecules are estimated with the help of thermal basis of electrical conductivity and dielectric parameters.

Graphical Abstract



Microphotographs obtained in between the crossed polars.

Keywords: Conductivity, Dielectric parameters, Space charge relaxation, Activation energy.

INTRODUCTION

The expansive ambit of relevance of liquid crystals across the realms of science and technology has led to for reaching exploration in this field of study. The materials are used in electro-optical devices, because of optical anisotropy of molecular orientation: which can control by an external electric field. Optical anisotropy of dielectric and opto-electrical characteristic traits are well known to employ the image quality of liquid crystal displays. Moreover the optical-birefringence of chromonic liquid crystalline phases is also important for fast switching display. For more advanced applications of quantum dot enhanced liquid crystal display, it is essential to understand the alignment of molecules of liquid crystals. The diverse thermo-optical parameters of liquid crystal substances provide necessary input to comprehend the interactive aspect between molecules [**1-5**].

In this paper, our aim is to study the space charge relaxation time and activation energy of different phase transition stages of different liquid crystalline phases such as cholesteric, SmA, SmC* SmC, re-entrant SmA and SmE sequentially when the specimen is cooled from its isotropic phase. Optical anisotropy of dielectric parameter, space charge relaxation and activation energy are helps us to understand: how the mobility of free charge carriers changes a different molecular structures depending on the internal molecular interactions. Electrical conductivity of liquid crystalline phase has also been incorporated.

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MATERIALS AND METHODS

In the current study, liquid crystalline used-cholesterol isobutyl corbonate(CIB) and 4-(trans-4'-hexylcyclohexyl) isothiocyanatobenzenes (6CHBT). The samples were blended and varied concentrations of the experimental mixture were left for duration of 6 hours in desiccators. Towards the end of stipulated period, in order to ensure homogeneity, the samples were exposed to many cycles of the process of heating, stirring and centrifuging. Optical-phase transition temperatures of the mixture were measured with the help of Gippon-Japan polarizing microscope in conjunction with hot stage. The samples were sandwiched between the slide and cover slip and they were sealed for microscopic observations. Electrical-conductivity measurements of the mixture at different temperatures were carried out using digital LCR meter and a proportional temperature control unit.

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.

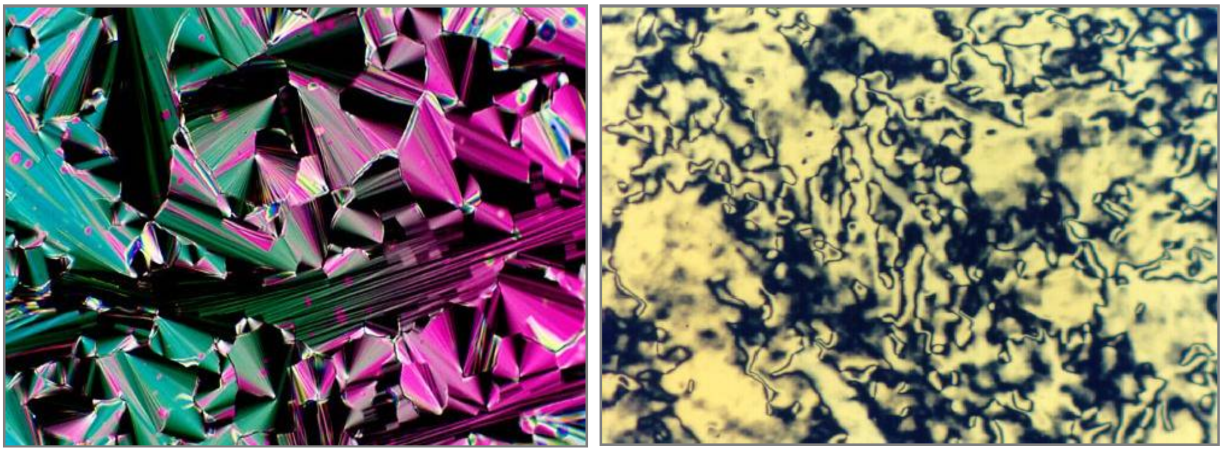
The loss factor is given by the following equation

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

Capacitance values were read up to three significant figures, and the values of the dissipation factor were recorded up to four significant figures in the present study. 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°C.

RESULTS AND DISCUSSION

Optical Texture Studies: Molecular orientations of optical textures displayed the samples were observed and recorded using the Gippon-Japan polarizing microscope in conjunction with hot stage. The specimen was taken in the form of thin film and sandwiched between the slide and cover glass. The concentrations from 20% to 80% of CIB in 6CHBT have been considered for the experimental studies. Binary mixture of50% CIB in 6CHBT is cooled from its isotropic melt and hence it exhibits cholesteric, SmA, SmC* SmC, re-entrant SmA and SmE phases sequentially. While the sample is cooled from its isotropic phase, the genesis of nucleation starts in the form of small bubbles growing radially, which are identified as spherulitic textures of cholesteric phase with large values of pitch. On further cooling the specimen, the texture slowly transform to focal conic fan texture of SmA phase in which the molecules are arranged in layers and the texture is as shown in figure 1(a). The SmA phase is unstable and then it changes over to SmC* phase, which exhibits radial fringes on the fans of focal conic texture of chiral SmC* phase. On further cooling the specimen, this phase slowly changes over to schlieren texture of SmC phase and as shown in figure 1(b). The SmC phase is also unstable and then it changes over to bubbles in the form of battonnets, which are the characteristic of SmA phase and this phase has been termed as the re-entrant SmA (ReSmA) phase [6, 7]. Sequentially on further cooling the specimen: the existence of re-entrant SmA (ReSmA) phase slowly changes over to herringbone pattern of SmE phase, which remains stable at room temperature and then it becomes a crystalline phase [8, 9].



Focal conic fan-shaped texture of SmA phase (250X). Schlieren texture of SmC phase (250X).

Figure 1. Microphotographs obtained in between the crossed polars.

Dielectric Parameters: The dielectric studies revealed information about molecular structure, molecular dynamics and optical-phase transition behavior and they are used as an input to its display applications [10, 11]. In addition; the dielectric anisotropy and dielectric loss of the liquid crystal arising from angular correlation between the molecules, not only through the light on the 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 50% of CIB in 6CHBT. The dielectric constant (ε')presented as shown in figure 2. From the figure, the discontinuities are observed; while the optical phase transition temperature changes a different liquid crystalline phases, they appear from cholesteric-smectic region. The dielectric parameter ϵ' decreases with increasing the temperatures, the most remarkable feature of this parameter 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 optical-phase transition from cholesteric-smectic region, the molecular twist can be of different liquid crystalline phases and it posses asymmetric to symmetric orientations towards the isotropic regions. A lateral property of molecular orientations gives rise to a positive dielectric anisotropy and hence it appears towards an isotropic region, the change in dielectric anisotropy remains uniform and it caused by the considerable longitudinal dipole moment. Here it may conclude that: the dipole moment exhibits an anti-parallel correlation in isotropic phase of given molecules [**12-23**].

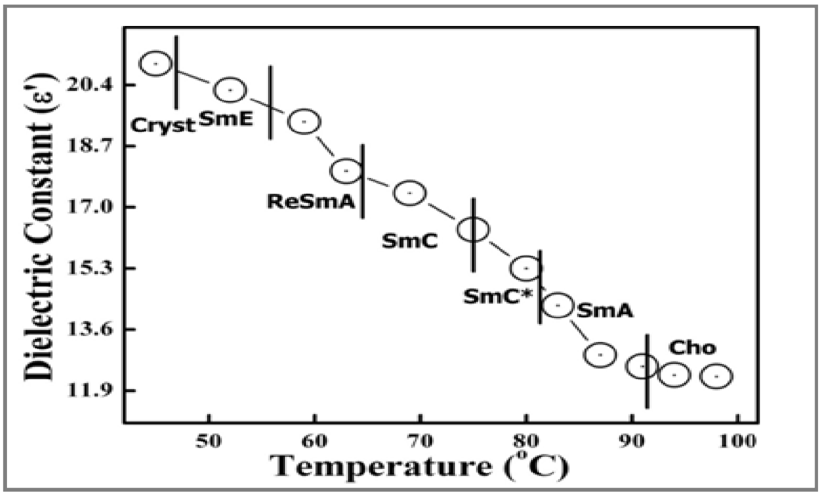


Figure 2. Temperature variation of dielectric constant for the sample of 50% of CIB with 6CHBT.

Conductivity Measurements: Electrical-conductivity measurements help in getting better idea on the phase transition behavior with temperature. An abrupt increase or decrease of electrical-conductivity with temperature relates to the phase behavior of lyotropic and thermotropic systems [**24**]. The temperature variation of electrical-conductivity for the sample of 50% CIB in 6CHBT is shown in figure 3. The changes were observed in electrical-conductivity, the values correspond to optical-phase transition system of liquid crystalline materials respectively at different temperatures and they were also identify the optical texture by the microscopic technique and hence it was observed that, the electrical-conductivity changes as we move from 98°C-91°C, 91°C-81°C, 81°C-74.8°C, 74.8°C-64.3°C, 64.3°C-64.3°C and 64.3°C-46.7°C, which correspond to phase transitions of Ch-SmA, SmA-SmC*, SmC*-SmC, SmC-ReSmA, ReSmA-SmE and SmE-Cryst phases respectively [**25, 26**]. Here it has been found that: the electrical conductivity goes on increasing as the temperature decreases: the increase in conductivity tells that, the orientation order has changes the little influence on its magnitude. This suggests that aggregated molecular size starts growing toward lower temperatures and then the system becomes more ordered.

Temperature Variations of Space Charge Relaxation Time on Cholesteric-Smectic-E Transition: The temperature variations of space charge relaxation time for the sample of 50% CIB in

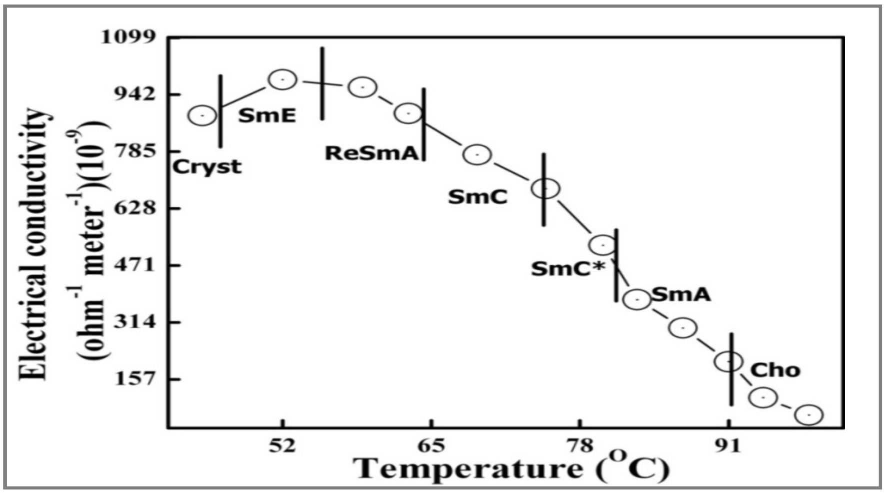


Figure 3. Temperature variation of electrical-conductivity σ (Ω^{-1} m^{-1}) for the sample 50% of CIB with 6CHBT.

6CHBT were analyzed through the corresponding Arrhenius-equation is shown in figure 4. From the figure it is observed that: the space relaxation times in solid phase are increased slowly and they are increase rapidly in liquid crystal phase to isotropic phase. By increasing the temperature, space charge relaxation process is faster. There is a jump at the optical-phase transition from crystalline phase to isotropic phase. The mobility of space charges move under the action of the external field and the resulting space charges produce a polarization which contributes to the total dielectric constant. A space-charge relaxation effect is important for evaluating the electro-optical response of thin-film-transistor liquid-crystal displays [27, 28].

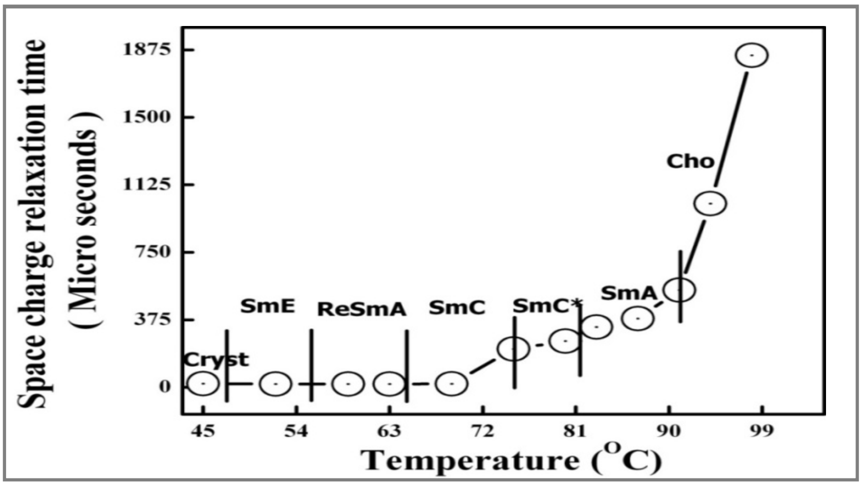


Figure 4. Temperature variations of space charge relaxation time for the sample of 50% **CIB** with 6CHBT.

Temperature Variations of Activation Energy on Cholesteric-Smectic-E Transition: Temperature variations of activation energy for the sample of 50% CIB in 6CHBT is shown in figure 5. The activation energy of relaxation transitions tells that: the energy of intermolecular interactions lead to the formations of free volume. The activation energy can be interpreted as the energy required to make the re-orientations of given liquid crystalline molecules and hence the energies are necessary to make the dissociation [29]. Relatively higher value of activation energy is the most suggestible higher potential barrier witnessed by the molecular dipole moment to orient at higher field. And hence to decrease in activation energy shows relatively higher and higher dielectric strength. From the figure it is clear that: the activation energy is increases with increasing temperature. The increase in activation energy shows the surface activity of dispersed particles on local order of the liquid crystal; the increase in activation energy which lead to restrict the mobility of free charge carriers and hence it has low conductivity. Consequently the decrease in activation energy of the given molecules shows the existence of higher mobility of free charge carriers as it move towards crystalline phases with increase in conductivity of the order of nano meter. The variation of activation energy is an effective way to improve optical properties of nematics or chiral nematics and hence it working in electrically-induced transmittance or selective light reflection modes.

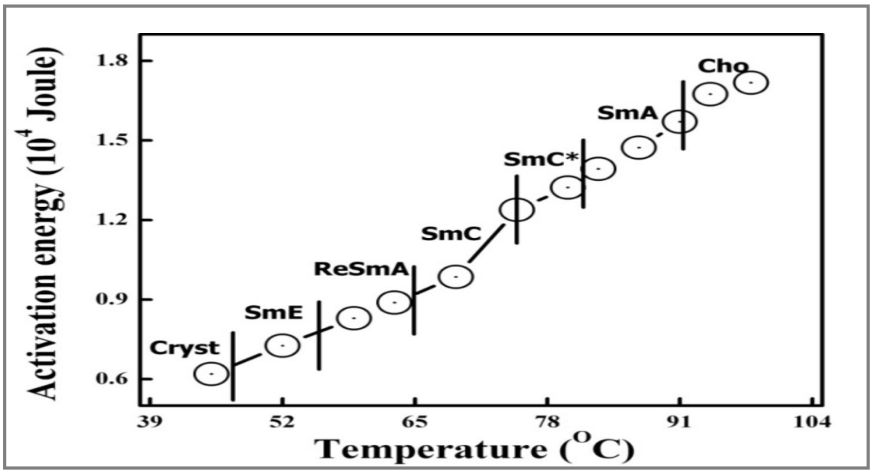


Figure 5. Temperature variations of activation energy for the sample of 50% CIB with 6CHBT

APPLICATION

This study shows how microscopic technique and optical anisotropy of binary mixtures of given liquid crystalline materials changes with variations of temperature.

CONCLUSION

Microscopic investigation of the binary mixture of CIB in 6CHBT shows the existence of cholesteric, SmA, SmC* SmC, re-entrant SmA and SmE phases for some concentrations of CIB. We observe that: the changes in values of dielectric and electrical conductivity studies with temperature unambiguously correspond to optical phase transition between cholesteric to smectic regions. By using then optical anisotropic technique: the space charge relaxation and activation energy are helps to understand the mobility of free charge carriers are more effective way to improve conductivity, the absolute values of conductivities as increasing in individual phase of liquid crystals towards the phase transition from cholesteric to induced smectic phases. It is the way to use the proposed structure as temperature sensing device, narrow band optical filter and in many optical systems.

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