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Electro Optical Properties of Cholesteric Liquid Crystal

Satyendra Pratap Singh*

Ph. D AIAS, Amity University, Noida, Uttar Pradesh, India

***Corresponding Author:** Satyendra Pratap Singh, Ph. D AIAS, Amity University, Noida, Uttar Pradesh, India,
E-mail: spsingh9@amity.edu*

ABSTRACT

The importance of liquid crystal is increasing constantly due to their wide spread use in display technology and other devices. Due to their possible opto-electronic materials with tunable optical properties are of great interest today. Mixtures of two different materials both of which possess tunable properties are very useful in forming such composites. It is known that properties of them depend on their shape, size and dielectric properties of surrounding medium. For application of any liquid crystal in practical device it must retain suitable values of certain parameters like dielectric permittivity, dielectric loss, conductivity, refractive index, birefringence and viscosity etc. with varying condition like temperature and electric field. Usually it is very difficult to fulfill these conditions with a single liquid crystal sample. Hence liquid crystal mixture has come to play an important role in device applications. We measure different parameters of mixtures of two cholesteric liquid crystal. From these values we find the various characteristics of liquid crystals.

Keywords: Dielectric constant, Dielectric loss, Conductivity, Refractive index

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INTRODUCTION

The Liquid Crystal (LC) state is matter's that state which stays in between solid crystals and isotropic liquids. LC's showing order in their orientation and not in positions. On the context of chemical composition, each and every liquid crystal has an aromatic ring with a aliphatic tail **(Figure 1)**. The aromatic ring gives required rigidness whereas the aliphatic tail provides the fluidity to the liquid crystals. So, this is an intermediate of solids and liquids. This phase is also known as "meso" phase [1,2].

LC phase is also known as MESOPHASE. Austrian botanist Friedrich Ritzier and a German Physicist Otto Lehmann discovered LCs in 1888 and are called Grandfather of LCs. This mesosphere are less like solid and more like liquid as their latent heat for transition for liquid is low, so to turn LCS to liquid lesser heat is required then to turn them into solids. This is the reason why the liquid comes first and crystal afterwards in LCs.

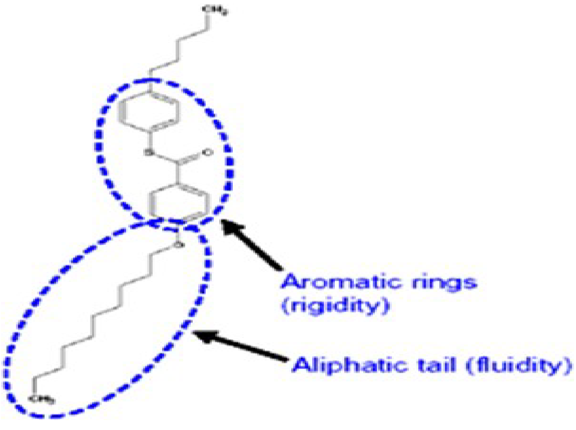

Figure 1: Liquid crystal chemical structure.

Due to their different structure they are very important material which is used in many applications these days. Their most important application these days are their use in display devices. They are also used in low-volume, niche products, such as spatial light modulators and generally as very fast light shutters. More importantly, they have come to dominate the displays market in portable instruments due to their slim shape, low weight, low-voltage operation, and low power consumption [3].

It has different physical and optical properties. Therefore, it is very important to know the physical, chemical, electro-optical and dielectric properties of these materials systematic study. This study gives a foresight in their various possible uses in near future.

The dielectric studies are very important to find the information about molecular structure and its molecular dynamics [4,5]. In addition to that dielectric anisotropy and dielectric loss of the liquid crystal arising from angular correlation between the molecules gives important information not only on individual molecular structure but also their ordering in a particular phase, which otherwise can be characterized by order parameter. As we that the values of dielectric permittivity and dielectric loss are changing in accordance with the variation of temperature, these parameters can be used to measure the transition temperature of not only the pure liquid crystals but also for their mixtures **(Figure 2)**.

Optical transmittance is also one of the important physical parameter. This is very important for finding the most crucial parameters of a display device, i.e. luminescence and contrast ratio [6]. Most of the researchers have concentrated their work on pure cholesteric esters [7,8]. However, some groups have reported data on Ch-Ch, Ch-N, N-N and Sm-Sm mixtures [9-12].

Similar to solids, mesomorphic compound's melting point is decreased by addition of another substance. The same is true in case of liquid crystalline materials. However, if the structure of added substance is not same to the original compound, there is only a small amount is enough to cancel the liquid crystallinity because of its cancelling effect on the mesophase [13]. If on the other hand the dopants are structurally similar, to original material liquid crystallinity may stable to a high concentration of the second component. In some cases, it remains for all compositions if both components are mesomorphic [14,15].

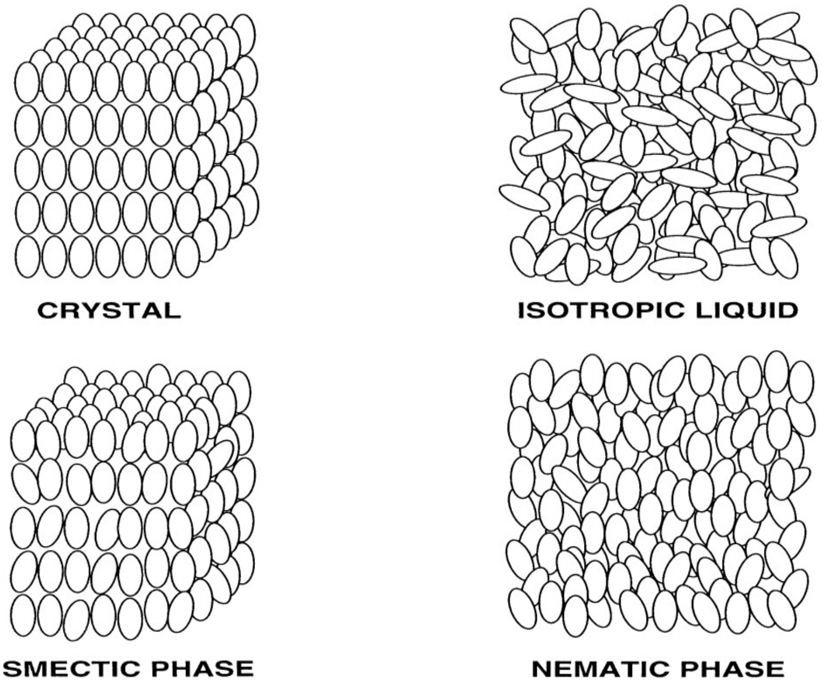

Figure 2: Molecular arrangement in the solid, liquid crystal and liquid phase.

Measurements of physical, electro-optical and dielectric factors of LC need a careful and qualitative study by using the proper experimental techniques. Here we describe all the techniques, starting from the fabrication of the sample cell to techniques which are used to find the material parameters, dielectric, and electro-optic response of LC samples.

Cholesteric liquid crystals show very clearly that molecular structure and external fields have a direct effect on their behavior and phase structure. Due to chirality of its molecules, they possess a super molecular periodic helical structure. The spatial pitch of cholesteric can be of the same order as the wavelength of visible light. Due to this Bragg reflection occurs. On the other side this helix pitch is very sensitive to the influence of external conditions. Their structure is like cholesterol molecules due to possession of a chiral center in this phase.

Molecules are found with slightly skewed orientation lie next to each other. Cholesteric LCs is also known as Chiral Nematic. Positional order is not present and Orientational order is found. Its structure is PITCH dependent. To make a complete turn required by the director is called PITCH; hundreds of nanometers make a single pitch. In these LCs only, concentration is responsible for phase transition. These molecules are composed of organic molecules in a highly polar solvent. Amphiphilic compounds as a solute and a polar solvent makes lyotropic crystals. Scientist has a great interest in these LCs and they are also vital as a technical point of view.

The cholesteric structure showing chirality occurs not only in pure compounds, but they are also present in mixture of achiral nematics with mesogenic or non-mesogenic dopants. Basically, the structure of cholesteric is very similar to nematic material. They are also called as chiral nematic LCs. The helix may be either right or left handed. It depends on the initial absolute configuration of the molecules. In some mixtures helix sign inversion is observed on changing the concentration or temperature.

EXPERIMENTAL TECHNIQUES

In this paper, the experimental techniques used to characterize liquid crystal (LC) materials and their properties have been discussed in detail. First, we see the techniques and material engaged in fabrication of LC sample cell. The fabrication includes which include deposition of transparent and conducting of ITO on film, photolithography, etching of desired pattern, treatments for desired alignment, assembling and filling of sample cell. Further, we studied various techniques for textural and electro-optical investigations. The various instruments used in studying the liquid crystals also read in detail. In the end some various physical properties of liquid crystal state are observed. The preparation of LC sample cells is one of the most significant steps in order to explore and understand the properties of LCs. These LC sample cell play a vital role in LC research because all experiments are carried out on these sample cells. This section explains all the steps used in cell fabrication. The process of cell fabrication generally divided into four major steps:

i. Deposition of transparent conducting of ITO coating on glass substrates,

ii. Photolithography and etching to attain the desired pattern,

iii. Surface treatments for LC alignment, and

iv. Assembling, sealing and filling of sample cell.

For coating on glass plates various materials can be used such as semiconducting oxides (oxides of tin, zinc and cadmium), and metals such as silver and gold. For this we require a transparent material which is our basic requirement. Because of which we can see the image of liquid crystals after filling LC's on it without any hindrance [8]. Now the other properties of the material which we shall prefer are its conductivity, thermal durability, etch-ability, work function, thickness, deposition temperature, uniformity, toxicity and its cost [9]. For this we use ITO i.e. indium tin oxide, this ITO have all the above-mentioned properties. The methods of its preparation include physical methods (sputtering, evaporation, pulsed laser deposition) and chemical methods, such as chemical vapour deposition etc. Here we used sputtering technique.

Photolithography is a process we used to transfer a desired pattern from a photomask pattern to the ITO coated glass substrate. The photomask is basically a transparent polymeric material with printed pattern on it. To achieve desired pattern on ITO substrate, one needs to follow the steps such as

i. Substrate cleaning and photoresist application,

ii. Soft baking,

iii. Mask alignment and UV exposure,

iv. Development and hard baking, and

v. Etching.

Since, the photoresist is UV sensitive, the whole process must be done in the dark room [13,14]. The diagrammatic illustration of steps involved in photolithography and etching to make the desired pattern on ITO coated glass substrates has shown in **Figure 3**.

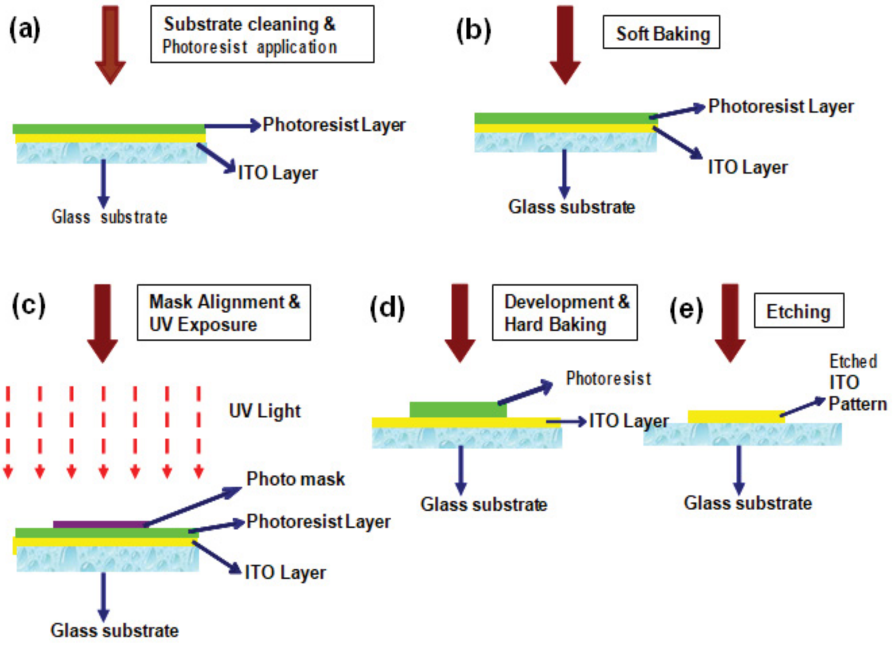

Figure 3: The schematic diagram of steps: (a) substrate cleaning and photoresist application (b) soft baking (c) mask alignment and UV exposure (d) development and hard baking, and (e) etching, to make the desired pattern on the ITO coated glass substrates.

Dielectric measurement

Both the dielectric permittivity (*ε'*) and losses (*ε''*) are measured with the help of a impedance/gain phase analyser of Hewlett-Packard type HP 4194A. To find out the real permittivity of sample is we εuse the change in capacitance value of the sample holder due to the presence of sample, by using the equation written as:

$$\varepsilon ?=\frac{\Delta C}{C_G}+1$$

Where ΔC, the change in value of capacitance of sample holder due to sample presence is given by

$$\Delta C=C_p-C_o$$

Where C_o and C_p are the capacitance without sample and the capacitance with sample. C_G here is the geometrical capacitance of our sample holder.

The loss factor is given by the following equation

$\varepsilon''=\varepsilon'\tan\delta$

Where $\tan\delta=\frac{C_pD_p-C_oD_o}{C_p-C_o}$ here D_p and D_Z are the dissipation with sample and the dissipation without the sample respectively. Here Capacitance values are read up to three decimal places. On the other hand, values of dissipation factor were recorded upto four decimal places in our present work. Constant temperature has been maintained throughout the entire experiment using a precise temperature regulator, Julabo F-25, giving an accuracy of ± 0.1°C.

Dielectric spectroscopy (DS) is one of the most frequently used modern method for finding the physical and chemical analysis of materials. The main reason for using this is ability of this method to find the relaxation processes of complex systems for an extremely large range of characteristic times ranging from 10^{-12} sec to 10^{5} sec. this is done by means of impedance analyzers [16], network analyzers as well as time domain spectrometers [17].

At higher frequencies, (above 10 GHz) wave-guides are used. This means that for each frequency a separate apparatus is necessary to perform accurate dielectric measurement. This technique is very sensitive for the intermolecular interactions and capable to monitor cooperative processes. It is made a link in between investigation of properties of the individual constituents of a complex material and its characterization of bulk properties with help of molecular spectroscopy.

Optical transmittance measurement

For finding the optical transmittance we placed LC cell with cross position on our polarizing microscope. This apparatus is fitted with hot stage arrangement. The light intensity which is coming through the sample is measured by a relevant e-o sensor at different temperatures. The samples texture image is captured by a camera connected to the one of eyepieces.

In optical method, a photodiode is used to measure the optical response of LC samples on a CRO. The time taken for change in optical transmission from 10% to 90% of maximum transmission gives rise time (τ_R) of the sample and the time taken for 90% to 10% decrease in transmission gives decay time (τ_D) of the sample. Thus, we can directly measure the optical response time (τ) on the time axis of CRO.

RESULTS AND DISCUSSION

To perform our experiment, we first observed the dielectric permittivity (ε') of our present sample at frequencies 1 kHz and 100 kHz and then their variation of dielectric permittivity for both pure sample and their mixtures of concentration 3:1, 1:1 and 1:3 during heating cycle are clearly shown in **Figures 4** and **5** respectively. For each sample what we clearly see is discontinuity in the values of dielectric permittivity from this we can say that there must be a phase transition.

There is value of ε' which increases continuously as we increase the temperature of it until it achieves cholesteric phase. Then it falls sharply. After further increase in temperature ε' decreases until isotropic phase is achieved. Then the values become almost constant. From this it is concluded that there must be a considerable freedom of dipole orientation in this type of liquid crystal phase of pure sample as well as their mixtures. Same type of behaviour is also observed by some other workers [18-20]. The values we found out of transition temperatures for Cholesteryl Pelargonate are 80°C and 92.5°C. The value for Cholesteryl Butyrate is found to be 94°C and 105.5°C.

These values are for crystal into cholesteric and cholesteric to isotropic phase transition respectively. From this, the change in value of ε' with temperature is very small for crystal phase as compared to the cholesteric phase.

When it has attained the cholesteric phase, then the values of (ε') decrease with increase of the temperature. The same kind of nature is clearly following the Onsager's relation [21]. The variation in dielectric permittivity (ε') in isotropic phase is very small like normal liquids, which is seen earlier also [5]. For low frequency values, the values of (ε') are bigger which clearly indicate that the dielectric relaxation, may be also happen at higher frequencies. But at the same time, it must be clear that no dielectric relaxation has been found in the frequency range covered in the present investigations.

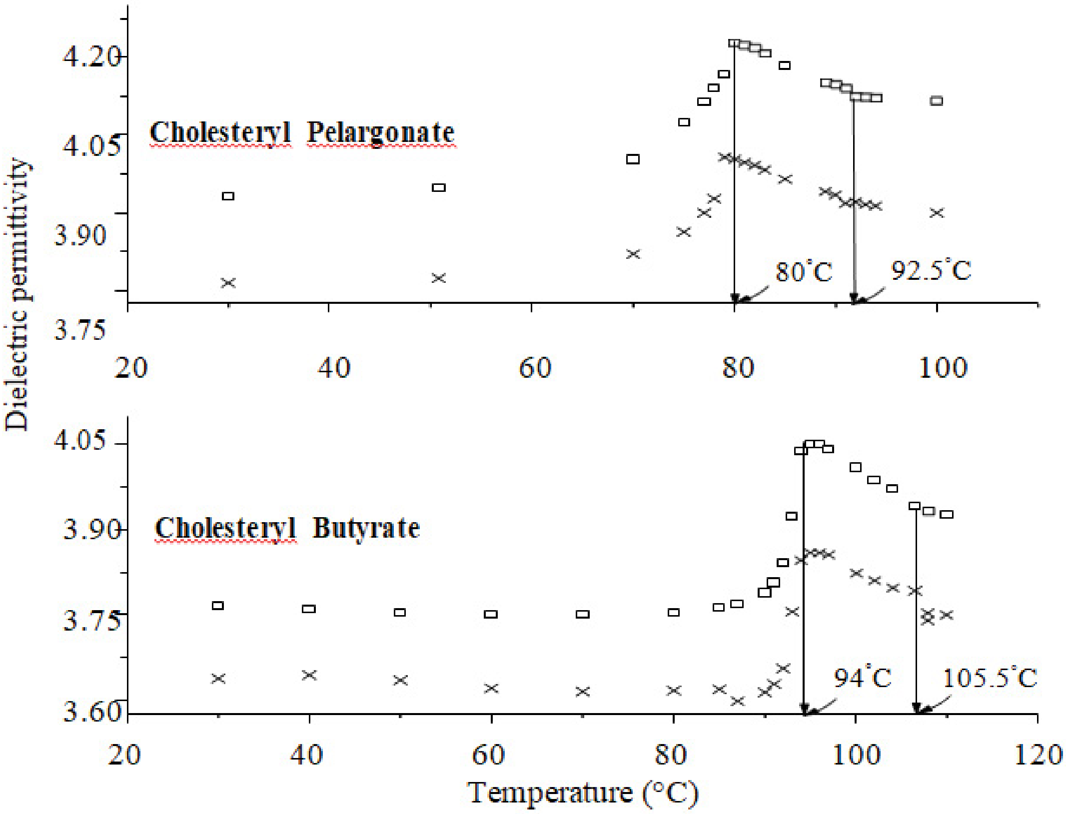

Figure 4: Temperature variation of dielectric permittivity for Cholesteryl Pelargonate and Cholesteryl Butyrate at frequencies 1 kHz and 100 kHz.

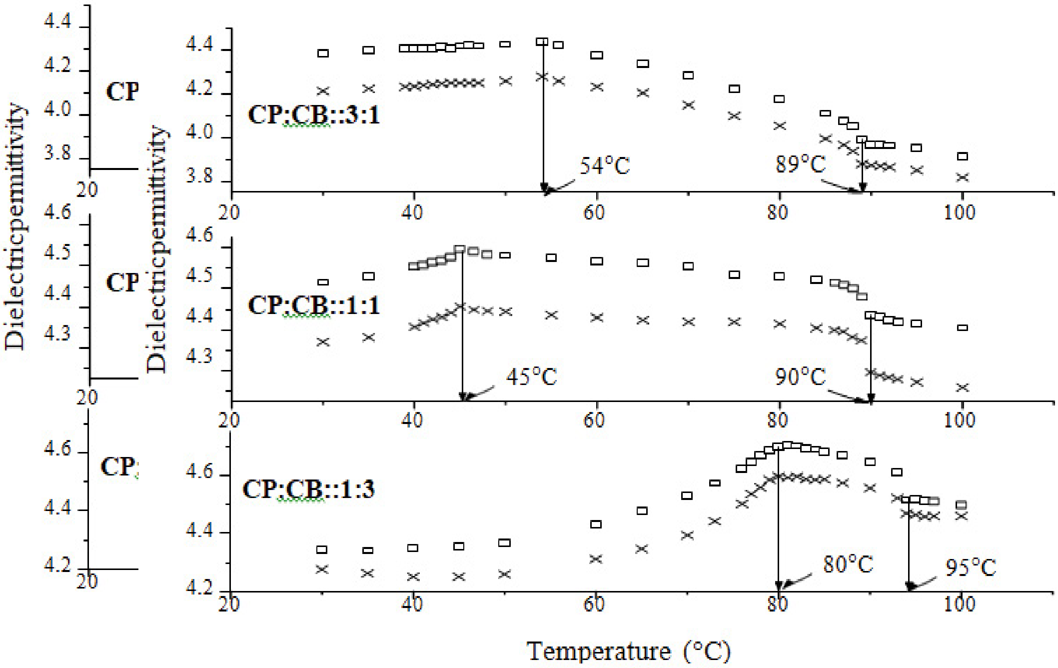

Figure 5: Temperature variation of dielectric permittivity for mixtures of Cholesteryl Pelargonate and Cholesteryl Butyrate at frequencies 1 kHz and 100 kHz.

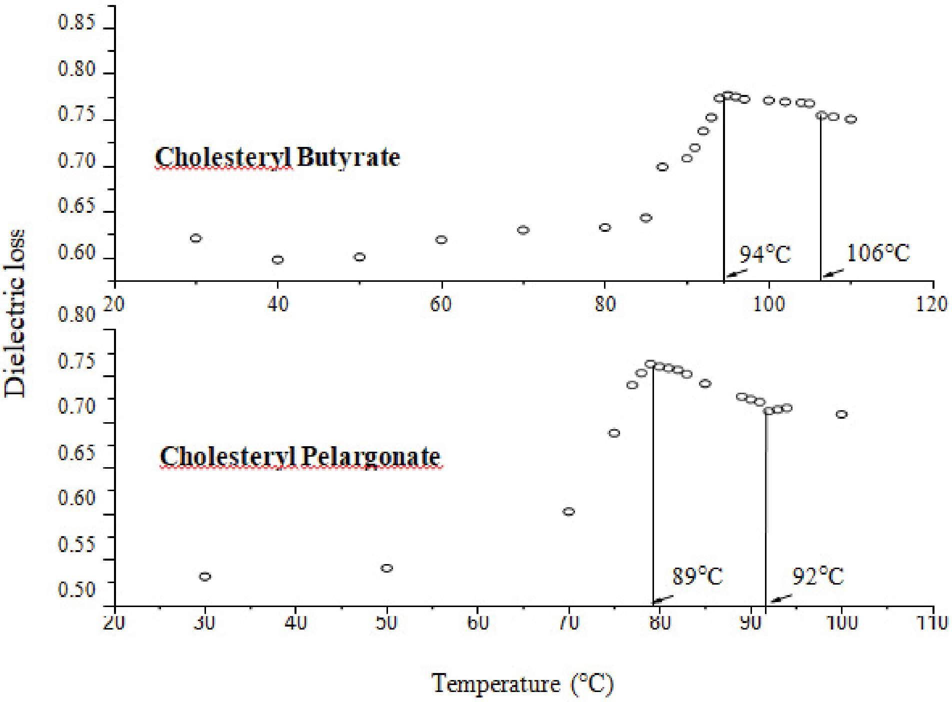

Figure 6: Temperature variation of dielectric loss for Cholesteryl Pelargonate and Cholesteryl Butyrate.

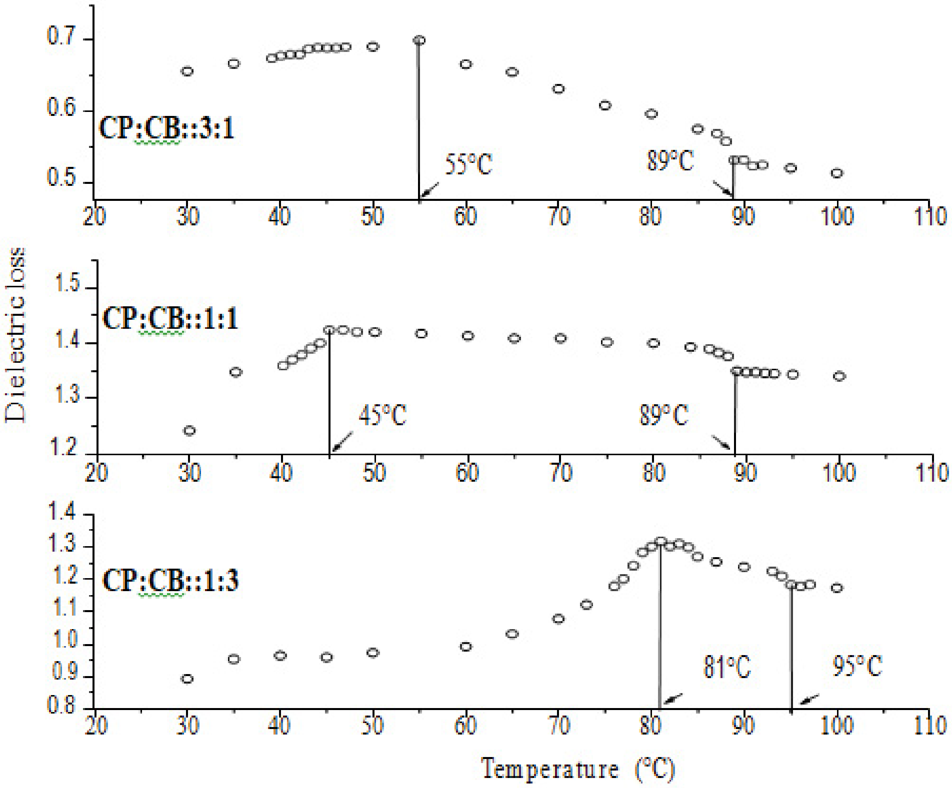

Figure 7: Temperature variation of dielectric loss for mixtures of Cholesteryl Pelargonate and Cholesteryl Butyrate of concentrations CP:CB::3:1, CP:CB::1:1, CP:CB::1:3.

The plot for dielectric loss against temperature is also find and which is shown in **Figures 6** and **7**. Variation of dielectric loss also shows the discontinuity at the temperature of phase transition. The phase transition temperatures values which were obtained from dielectric loss study are similar with those obtained by dielectric permittivity study which was expected.

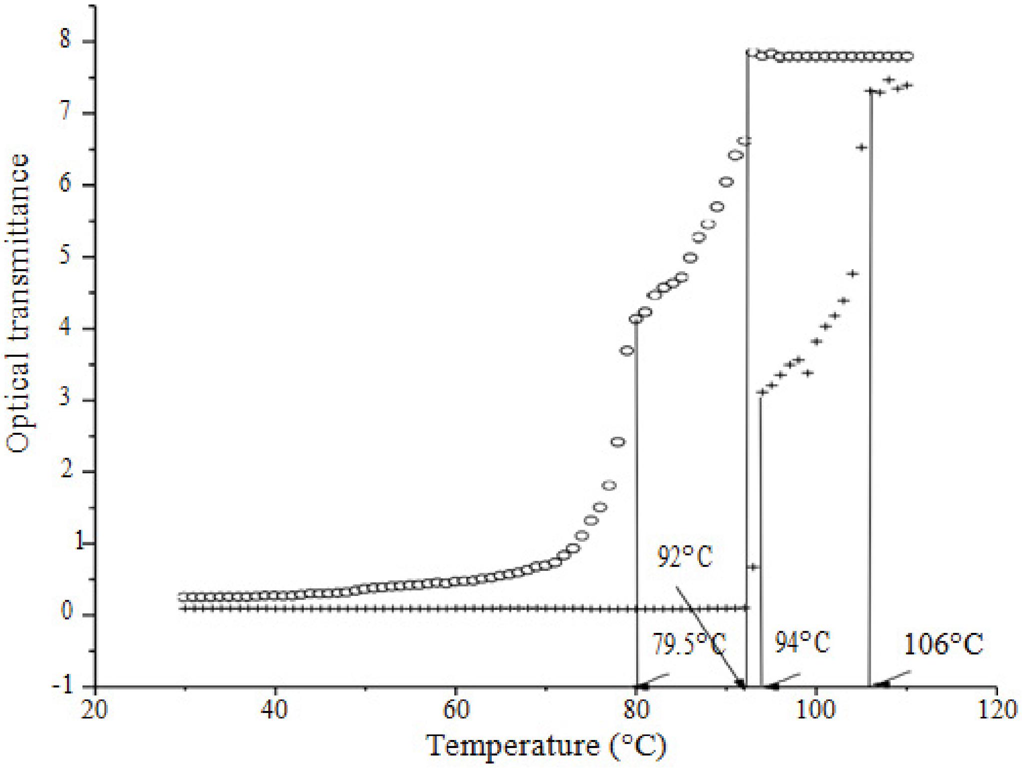

Figure 8: Plot of temperature variation with optical transmittance for Cholesteryl Pelargonate and Cholesteryl Butyrate.

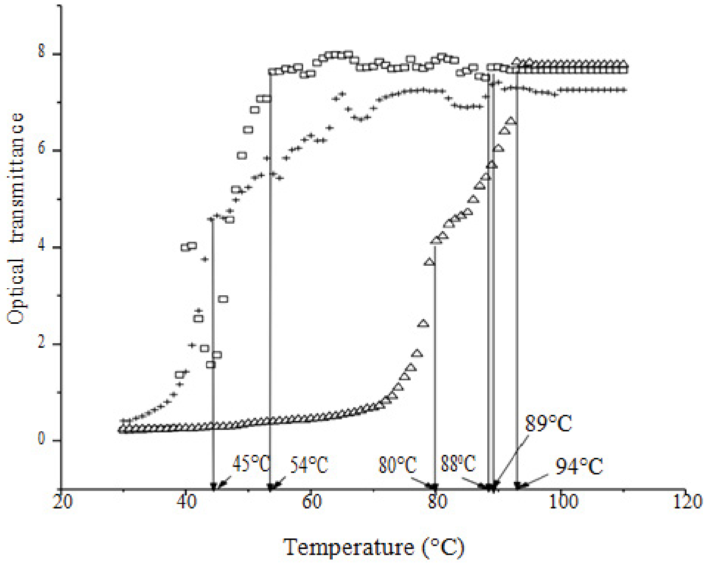

Figure 9: Plot of temperature variation with optical transmittance for the mixture of Cholesteryl Pelargonate and Cholesteryl Butyrate of concentrations CP:CB::3:1, CP:CB::1:1, CP:CB::1:3.

Figures 8 and **9** are showing variation of the optical transmittance in arbitrary unit against the temperature for both pure samples and their mixtures respectively. The optical transmittance value which has been found constant in the crystal phase and then increases as we raise the temperature also shows a sharp change during the crystal to cholesteric transition for different samples. The Optical transmittance attains a maximum value of phase transition temperature at cholesteric to isotropic phase. After that temperature this remains nearly constant on increasing in temperature. This kind of nature is almost similar for all samples which having different transition temperatures.

It is clear from **Figure 8** that at 79.5°C Cholesteryl Pelargonate shows a crystal to cholesteric phase transition. Under this cholesteric phase its value is greater as comparison to its value measured before its transition from crystalline phase to cholesteric phase. Optical transmittance value firstly increases with a constant rate before attaining a constant value at 93°C which shows that sample transform into an isotropic phase. The behaviour For Cholesteryl Butyrate's optical transmittance is similar as that of Cholesteryl Pelargonate but its transition temperatures are found to be at 93.5°C and 106°C respectively for S-Chiral and Chiral-Isotropic phase transition. In **Figure 9**, transition study of mixture CP:CB::3:1 is shown. Which indicates a sudden increment in optical transmittance value at 54°C indicating S-Ch phase transition and then it increases to reach the maximum value at 88°C indicating Ch-I phase transition temperature. For mixture of CP: CB::1:1 and CP:CB::1:3 the phase transition temperatures are found to be 44.5°C, 89.0°C and 80°C, 94°C for S-Chiral as well as Ch-I phase transition respectively. The values obtained by different studies of two phase transition temperatures for pure as well as mixtures are placed and compared. These are found to agree well with each other.

It is an important point to note here that during our work we do not able to find any blue phase. This phase is considered as a specific form of cholesteric phase by some authors and as a separate form by others [22]. This blue phase is appearing in a very narrow temperature range just before reaching the isotropic phase. In our present work we may have missed the clear appearance of blue phase due to two probable reasons. First, the technique which we used to find the optical transmittance is lacking the facility of changing the wavelength, so absorption at Bragg's wavelength is not seen which may be indicate the blue phase.

Secondly, the sample enters the blue phase only for a very small range of the temperature which is very close to Ch-I phase transition. This is clearly a predominant phase transition at that point. So, the change observed in the parameters for Ch-I phase transition may superimpose on the change which is due to blue phase.

CONCLUSION

From the measurement of dielectric permittivity (ε') and dielectric loss (ε'') with the optical transmittance we are able to find the phase transition behavior of liquid crystal material. The mixtures which produced by single samples having own phases. We also learn to calculate the various electro-optical properties of cholesteric liquid crystals. Further, it is important to note that the non-linear behavior which we see in binary systems find in our present work shows that some there is molecular combinations takes place. This happens especially when mesophase is enhanced; this shows that for such molecular complexes thermal stabilities values is higher. An energy consideration is also a part of it.

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