OVERVIEW

This chapter covers the dielectric spectroscopy and electrical studies of three ferroelectric liquid crystal mixtures to study the basic thermodynamic properties of these materials. Depending upon the length of pitch as compared to thickness of the sample, the FLC mixtures are found to possess different electro-optic geometries. The mixture having long pitch as compared to sample thickness had surface stabilized and other two with short pitch were in deformed helix and short pitch bistable ferroelectric structure for weak and strong surface treatment respectively. In dielectric spectroscopy, the temperature, frequency and bias dependence of complex dielectric permittivity of these mixtures is studied. The results confirm the presence of various relaxation modes: Goldstone mode “GM”, Soft mode “SM, Bulk domain mode “BDM” and new relaxation mode “NRM”. The GM and SM are connected to the director fluctuations. In the SmA phase the system exhibits the degenerate mode i.e. (soft) mode only. Due to limited frequency window we could not observe the polarization modes. The BDM and NRM generally appear on application of field and are noticeable in thin samples (3μm). The relaxation frequency and dielectric strength of these modes have also been calculated and their variation with temperature is reported in this chapter.

In electrical studies, the polarization switching and dynamics of helix winding and unwinding have been investigated by applying triangular and square wave pulses. The parameters like spontaneous polarization, response time etc. have been measured using different techniques. The response time measurements performed by different techniques have been compared.

Dielectric as well as electrical properties depend upon the thickness and surface properties of the films. Effect of surface forces on above parameters has been discussed in these three mixtures and is explained on the basis of structure-property correlation. Theoretical model are framed to explain the results.

The effect of CNTs on these material parameters is studied and results are explained with possible theoretical estimations. The effect of CNT on the dielectric properties of FLC mixture shows a decrease/increase in permittivity in the SmC* phase depending upon cell geometry whereas the effect seems to be same in all cells resulting in increased value of permittivity at temperature near the transition temperature and well in the SmA* phase. The value of polarization is also observed to decrease/increase in SmC* Phase for different cell geometry. The value of response time and viscosity however decreases in all the samples. The reduction of response time has an industrial importance. The theories have been presented to explain the effect of CNT in these material parameters.
4.1 Review of Literature

4.1.1 Dielectric Studies

Before the discovery of ferroelectricity by Robert B Meyer (1975) the study of the liquid crystals was confined only to the nematic and cholesteric liquid crystals. Since no collective mechanism can be excited using dielectric spectroscopy in nematic and non-chiral smectic liquid crystals using dielectric spectroscopy, It came in picture only after the discovery of ferroelectric phases. Thereafter, number of research workers have studied the dielectric properties of Nematic and FLC mixtures and its dependence on temperature, frequency, pressure etc (Raina et. al. 1999 & 2000, Hudak et. al. 1983 Kimura et. al. 1993, Panarin et. al. 1994, Markscheffel et. al. 1996). Some of the efforts have also been made to probe the structure of the material with the help of dielectric measurements e.g. different possible dipolar orientations at the surface in the thin film cells. However, the main outcome has been the characterization of the dielectric properties of the \textit{GM} in the SmC* phase and \textit{SM} in the SmA and SmC* phases (Lagerwall et. al. 2002, Zeks et. al. 1988, Carlsson et. al. 1988 & 1990, Fillipic et. al. 1988, Urbanc et. al 1989).

Pikin et al. (Lagerwall thesis 2002) and Blinc et al. (Lagerwall thesis 2002) predicted theoretically that the dielectric permittivity exhibits a cusp like behavior near the transition temperature, using the Landau free energy density model. However, this early way of representing the free energy expansion failed to describe the experimental behaviour of the system properly. Experimentally the permittivity show a pronounced increase near the transition to the SmA phase. The maximum value of the permittivity is not observed at the $T_c^{+A}$ as predicted by the theory. The model failed to accurately define the dependence of pitch and ratio between polarization and tilt angle on temperature. Later, Zeks, Carlsson, Fillipic and Levestik etc. (Zeks et. al. 1988, Carlsson et. al. (1988) 1990, Fillipic et. al. 1988, Urbanc et. al. 1989) modified this model using generalized Landau expansion. The most important feature of the generalized Landau model is the presence of a biquadratic coupling term between tilt and polarization in the free energy density of the system. Using this model, they presented a complete description of the temperature and frequency dependence of the complex dielectric permittivity. They have shown how the general thermodynamic and dielectric properties of the system
depend on the strength of the coupling. They also reported that the SM and GM are actually coupled through the amplitude fluctuations, which enter both modes, but as a good approximation (except very close to $T_c$) this mixing can be discarded since the phason susceptibility is much higher than that of the amplitudon.

Since, no attempt was made by Carlsson, Blinc and Zeks 1988 to explain the GM and SM due to the fluctuations of the polarization order parameters, Carlsson et al. 1990, later, discussed it in some more detail. They resolved the permittivity in to four modes and derived the relations for the dielectric strength and relaxation frequencies of all the collective modes in the SmC* as well as SmA phases, subsequent to certain assumption. They consider that as the polarization fluctuations are much faster than the director fluctuations in SmC*phase, director is fix while studying the fluctuations due to polarization and the polarization being stable as its average position when studying the director fluctuations.

Levstik et al. (1987) measured the complex dielectric constant at a room temperature FLC mixture BAHABAC. Authors resolved the complex permittivity into GM and SM and determined the dielectric strength and the relaxation frequency corresponding to each mode. The results were compared with those calculated theoretically using the generalized model of Landau expansion. It was observed that the theoretical calculations were able to describe the experimental data as well. Filipic et al (1988) have shown that for the materials having large spontaneous polarization, the contribution from the GM and SM can be resolved in comparatively large temperature interval in the SmC* phase close to the transition to the SmA phase. Wrobel et. al. (1989) have reported that, however, the total dielectric constant contains both the modes, the SM decreases sharply and its studies were limited to a very narrow temperature interval in the SmC* phase below the transition temperature from SmC*.-SmA ($T_{C*-A}$) phase. This problem is not encountered in the SmA phase due to the absence of GM in this phase. This difficulty of resolving SM in SmC* phase can be overcome by the using a bias field perpendicular to the smectic layers. In this way helix is unwound and thus the contribution of the GM is eliminated.

Biradar et al. (1989) studied the dielectric properties of a room temperature FLC in the frequency range from 5 Hz to 13 MHZ. It was found that in the homogenously aligned sample two dielectric relaxation regions have been observed in the SmC*
phase. In homeotropically aligned sample a low frequency relaxation was observed in both SmC* and SmA phases attributed to the re-orientation around the short axis. The temperature dependence of the dielectric strength and relaxation frequency suggests that the system exhibits a phase transition of the first-order type.

Dielectric studies carried out on the fluorinated compounds having strong dipole moments attached to chiral centres and highly ordered phase showed the presence of the four relaxation modes in the SmC* phase (Biradar et al 1996). Wrobel et al. (1992) reported the presence of new relaxation mode known as new ferroelectric domain in a single component highly fluorinated compound where this mode is quite strong. This mode is connected to the formation of a special kind of modulated structure due to the tendency of the macroscopic polarization of smectic layers to compensate each other. Gouda et al (1992) proposed a model for the determination of the dielectric biaxiality in the in the SmC* liquid crystals having an uncompensated helix. This model is useful for determining correlation between the molecular structure and dielectric properties. Measurements were performed on one ester compound exhibiting A* and C* phases at different temperature and frequency.

Zubia et al. (1991) also reported the existence of a new relaxation mode in addition to the SM and GM having low relaxation frequency. They related it to the defect structure present in the samples with planar alignments. Beresnev et al. (1992) reported the new relaxation processes in FLCs with considerable high $P_s$ (FLC-243, 150nC/cm$^2$; FLC-247, 160 nC/cm$^2$; FLC-250, 150 nC/cm$^2$; FLC-270, 190nC/cm$^2$; FLC-271, 150nC/cm$^2$; FLC-273, 105nC/cm$^2$). It was explained that this new relaxation process ($DM$) is connected to the presence of new domain structure. They also reported that this $DM$ could only be observed in the absence of the classical ferroelectric helix.

K. K. Raina (1987) explained the helix dynamics studies carried out in the FLC compounds DOBAMBC and DOBAMBCC in ac fields from 0-20kHz. Two relaxation processes: “Slow” relaxation and a “fast” relaxation were observed, having typical relaxation frequencies 400Hz and 1kHz. Later, Raina et al. (1998 & 1999) Gathania et. al. (1999) have also proved the existence of a new relaxation mode in the ferroelectric liquid crystals.
Kuczunsky et al. (1990) have studied the influence of the electric field on the GM and SM in a FLC (4-octyloxy 4 -[(2 methylbutyloxy) carbonyl] phenylbenzoate) by optical method. They have also proved that the optical method is better indicator of the phase transition than the dielectric method. The soft mode peak was used as an identification of the phase transition. Their results suggest that these modes show complex behaviour and the applied electric field not only quenches the GM, but also strongly modifies the properties of the SM. It broadens the maxima and shifts it towards the higher temperature. However DC field does not affect the transition temperature. They also discovered new mode appearing in both SmA and SmC* phases. It’s relaxation time was independent of temperature and couples to the GM in SmC* and SM in SmA phase.

Levstik et al. (1990) gave an alternative method based on dielectric measurements on thick samples for determining the GM rotational viscosity and twist elastic constant of ferroelectric SmC* LC. Gouda et al. (1989) also measured the rotation viscosity and elastic constant using the dielectric method. Srivastava et al. (1993) reported the dielectric spectroscopy of a small pitch and high P$_S$ FLC-202 mixture with planar texture in the frequency range 100Hz-1MHz as a function of temperature and varying dc field in the SmC* and SmA* phases. Authors have evaluated the rotational viscosity and elastic constant from observed data.

Kalmykov et al. (1994) derived relation between the dielectric and electro-optic parameters of the liquid crystals materials and determined its response time from the dielectric strength and relaxation frequency of the GM.

Besides the ferroelectric liquid crystals we also have polymeric, oligomeric and banana shaped liquid crystals materials. Polymeric liquid crystals have slow responses and were not found suitable for the displays. However the oligomers were having properties in between the properties of ferroelectric liquid crystals and polymers i.e. fast response and glass transition temperature (Blatch et al. 1997, Imrie et al. 1998).

Now a new type of liquid crystals materials known as the banana shaped liquid crystals are proven to show ferroelectricity even in the absence of chirality. Till now only the structure and electro-optic properties of these materials are studied. No attempt has been made to investigate the dielectric properties of these materials (Sekine et al. 1997 & Sekine et al. 1997).
4.1.2 Electrical Studies

Ferroelectric liquid crystals are those chiral smectic phases in which the molecules have permanent dipole moment perpendicular to their long axes. So, materials parameters like polarization, response time etc. are studied for these FLCs. Clark and Lagerwall (1980) have proposed an attractive idea for the FLCs to work as a microsecond device. Handschy and Clark (1983) studied the switching mechanism by applying a pulsed voltage by spectroscopic technique with N₂ Laser. Ishikawa et al (Jasjit Ahuja Thesis 2000) studied by using a video stem to monitor under a low frequency (~0.1Hz) triangular voltage wave. The molecular reorientation process associated with switching mechanism is very complex and has strong dependence on many factors such as cell thickness, surface conditions, molecular alignment, temperature etc. However, the major factors, which define the speed of response for FLC electro-optical devices, are spontaneous polarization (Pₛ) and rotational viscosity (γₚ).

Different techniques like Sawyer-Tower procedure, the pyroelectric method and current reversal methods can be used to measure the spontaneous polarization (Blinov et al. 2000, Madhumohan et al. 1999, Bawa et al. 1987 & 1990, Raina et al. 2001, Srivastava et al. 1993). The pyroelectric technique offers the high accuracy for measurement of spontaneous polarization, but it is complicated and time consuming. The Sawyer-tower method is rapid but allows only the Pₛ measurements. The third technique involves the analysis of output voltage obtained through a standard capacitor or resistor and is most widely used. Rotational viscosity is measured using current repolarization method and electro-optical procedures.

Miyasato et al 1985 observed the current due to polarization realignment under a triangular voltage wave give direct information of the molecular re-orientation and determine the spontaneous polarization accurately. Later, Skarp et al 1987 estimated polarization, response time and rotational viscosity in single experiment using field reversal method. Ishikawa et al (Jasjit Ahuja Thesis 2000) have observed the double peaks in the current signal on application of triangular wave to the thin mono-domain cell. Ouchi et al (1988) have also observed the two peaks in the current signal of thin samples by triangular wave method. The peak that rises below 0V originates from both surface and interior molecular reorientation associated with the
transition from a uniform state to twisted one and the second peak is related to subsequent change to another uniform state.

Bawa et al (1987) have studied the dynamics of helix winding and unwinding processes under an applied electric field in ferroelectric liquid crystals by using a biased asymmetric square wave pulses. The molecular reorientation mechanism taking place in these processes have been compared with the switching processes amongst the two stable states of FLCs. They showed that the helices unwinding processes, which take place under the constraints of applied electric field, are much faster than the winding processes, which occurs naturally depending upon the viscosity of the material.

Later, Bawa et al (1988) have also studied the helix dynamics using symmetric and asymmetric triangular and square wave pulses. The square wave method is found to give direct measurements of the response time.

Bawa et al (1986) have measured the response time of the FLC using triangular waves of different frequencies. They showed that the peak due to polarization reversal shift along the abscissa axis with change in frequency and this shift is due to the response of the surface and interior molecular re-orientations.

Vaksman et al (1992) have measured the various parameters of the FLCs in a single experiment by using capacitor in current reversal method using square wave. They have also measured the azimuthal angle, dielectric anisotropy as well as complex dielectric constant along with the $P_s$, $\gamma_6$ and response time. V. Panov et al (2001) have also used this method for the measurement of material constants. A method for the measurement of DC conductivity is also presented in this paper. Samriti et al (2004) have proved that this method is more reliable for the measurement of response time.

Kalmykov et al (1994) have measured the response time of the materials by using the dielectric parameters of the Goldstone mode of the sample. The response time obtained by using this method is in accordance with those obtained for the current reversal techniques. Dielectric strength and relaxation frequencies of the GM are used to measure the response time.

Jakli et al (1996) have shown that in short pitch FLCs, low field only distorts the helix and large field unwind the helix properly giving a quasi bi-stable switching. In the intermediate field range where the system is in mixed state, in some areas the
helix remains stable whereas in other areas the switching takes place between the two unwound states.

Raina et al (1995) have studied the electro-optic properties of surface stabilized and deformed helix FLCs and proved that the surface stabilized configuration shows surface switching whereas DHF configuration shows surface as well as bulk switching. The properties of DHF have been studied in the cells of various thickness (2.5-7.5 µm) and observed that the surface switching is more dominant in the thin cells due to strong surface forces.

In SmC* phase the polarization P is proportional to order parameter $\theta$. The optical techniques have been found useful for measurements of $\theta$ in both planar as well as homeotropic geometry of the sample cell. The optical tilt angle is found by unwinding the helix in planar geometry using bipolar dc voltage or low frequency ac voltage (Markscheffel et. al. 1990, Wrobel et. al. 1995). The extinction position between the two completely switched states is observed and this gives a measure of tilt angle. In homeotropic geometry, the helix is unwound by applying electric field larger than the critical field $E_C$ in the plane of the smectic layers. For large electric field uniform texture is obtained with the molecules perpendicular to the field and tilted by the angle $\theta$ compared to the layer normal.

Now more elaborated method are discovered to measure the tilt angle of the materials. Etxembaria et al (1987) have determined the tilt angle of the liquid crystals using advantage of Wood and Glazer rotating analyser method for birefringence measurements, together with strong coupling of molecular director to the applied field in ferroelectric liquid crystals.

### 4.1.3 Guest-Host Effect

Some of the workers have studied the effect of guest in nematic and FLCs. The guest may be dye, ions or CNTs. Samriti et al have studied the effect of dye on DHFLC. They have also presented a theory to explain the results. Arvind et. al also studied the effect of dye on SSFLCs.

The effect of CNTs on Nematic and FLC has started recently. The field of carbon nanotubes (CNTs) has drawn a great deal of interest in fundamental and applied research since their discovery by Iijima in 1991, because they possess fascinating electrical, dielectric, thermal, mechanical, and electronic properties. The CNTs have
proved their importance in employing the devices as field-effect transistors (Martel et al. 1998), memory storage devices (Rueckes et al. 2000), sensors and actuators (Kong et al. 2000, Yu et al. 2006), and field emission sources (Baughman et al. 2002). The doping of CNTs, either single walled (SW) or multiwalled (MW) in liquid crystals (LCs), in order to have fast electro-optic devices, has been pursued by various groups around the world for improving their electro-optical properties (Lee et al. 2004, Chen et al. 2007, Jeon et al. 2007, Lu et al. 2008), dynamic response (Jeon and Park et al. 2007), and other physical parameters (Baik et al. 2005, Chen et al. 2006). But much of the reported work has been focused on nematic liquid crystals (NLCs) (Chen et al. 2007 & 2006, Jeon et al. 2007, Lu et al. 2008) and twisted NLC (Lee et al. 2004, Baik et al. 2005). The doping of CNTs in ferroelectric liquid crystals (FLCs) is rarely reported in literature. It has also been found that thermotropic (Lynch et al. 2002, Dierking et al. 2005, Scalia et al. 2008 & 2007) as well as lyotropic (Scalia et al. 2008) LCs have been used as a solvent providing a simple, versatile, and reproducible way to control the order in SWCNTs and MWCNTs. Some studies have been carried out on the translational motion of CNTs dispersed in NLC under an ac and in-plane field (Srivastava et al. 2007, Baik et al. 2006). Among many intrinsic physical parameters of LC material, the response time is the most important for addressing the fast LC display devices. Lee et al. (2004) demonstrated the effect of CNTs on LC to improve the switching behavior. Faster electro-optical response characteristics of carbon nanotubes-nematic suspension have been studied by Chen et al. (2007). The CNTs-doped LC optically compensated birefringent cells were studied by Lu and Chen (2008) for improvement in response time. The deformed helix FLCs (DHFLCs) are very useful and have much applications in display devices because of their low driving voltage, gray scale generation capability, easily achievable alignment, fast response, etc. (Bersnev et al. 1989, Funfschilling et al. 1989). The bistability or memory effect has also been demonstrated by Kaur et al (2004) in DHFLCs.

In India nowadays, Nanomaterials are considered to be a topic of current research. However as per our literature review only one (Kaur et al 2004) group in NPL, New Delhi, India is working on Nanocomposites with Liquid crystals as host materials with main emphasis on CNT dispersion. Various research groups from all over the world are engaged in study of these. Their main emphasis is on studying the
behaviour of these materials under influence of bias, light and by adding the solvents.

4.2 Experimental

4.2.1 Materials Studied

The dielectric and electrical studies are carried out in Three ferroelectric liquid crystal mixtures, FLC-6304, SCE 8 and FLC-827 respectively termed as FLC-I, FLC-II and FLC-III.

- FLC-I mixture has short helical pitch (~0.34µm), large spontaneous polarization (~110nC/cm²) and large tilt angle 27° at room temperature. It has a wide SmC* phase from -20°C to 59°C followed by a SmA phase (from dielectric spectroscopy) (Hoffmann La Roche, Switzerland).

- FLC-II mixture has long helical pitch 11-12µm, small spontaneous polarization (~6 nC/cm²) and large tilt angle at room temperature. It has a wide SmC* phase from –20°C to 60°C followed by a SmA phase (from dielectric spectroscopy) (Hoffmann La Roche, Switzerland).

- FLC-III mixture has short helical pitch large spontaneous polarization (22 nC/cm²) and large tilt angle 21 °C at room temperature. It has a wide SmC* phase up to 60°C followed by a SmA phase (from dielectric spectroscopy) (Hoffmann La Roche, Switzerland).

For dielectric measurements we used cells of thickness 6 µm prepared by phololithography technique (Von Hipple, Dielectric Relaxations). To study the effect of thickness, the cells of 100µm, 62.5µm, 25µm and 7.5µm were also used. The desired conducting area (square in shape) was 0.45 x n0.45 cm². The cells were calibrated using air and benzene as standard reference media and stray capacitance was removed. The material was then filled in these cells by capillary action at or above the isotropic temperature. A well-aligned texture was obtained by cooling the cells @ 0.1°C per minute using custom built temperature controller cum hot stage. The micro-textures of the samples were visualized through the polarizing microscope interfaced with computer. The procedure for preparing these cells is discussed in Ch. 2.
The guest–host effects are also studied for these mixtures. We have doped these compounds with different concentration of MWCNTs [BDH]. The MWCNTs used were synthesized at National Physical Laboratory (NPL), India by chemical vapour deposition method. The diameter of synthesized MWCNTs ranged from 30-50 nm with typical length ranging from 0.3 μm to several μm. The FLC -CNTs dispersion was prepared by adding small amount (0.2 wt%) of CNTs to materials followed by mixing.

Impedance analyzers 6540 A (Wayne Kerr, U. K.) and 8110G (Instek, USA) were used to measure dielectric permittivity of the samples in the frequency range 50 Hz–10 MHz. The results were found to be reproducible. The electrical properties of FLC-I have also been studied. The electro-optic measurements were taken by current reversal method using triangular and square waves. The output was studied on an oscilloscope interfaced with computer. The measurements were also done directly with Waynekerr LCR Meter. The details of experimental set-up for the dielectric and electrical measurements are provided in Ch3.
Part –1

FLC-I

FLC-6304

Geometry

**Deformed helix Ferroelectric Liquid Crystal mixture**

Due to the large sample thickness to helical pitch ratio \((d_s >> p_0)\), and small pitch as compared to the wavelength of light used we consider that the cell is in the deformed helix ferroelectric liquid crystal state

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Transitions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure FLC</td>
<td>Cr- -20°C-SmC*- 59°C-SmA</td>
</tr>
<tr>
<td>FLC+0.2% CNT</td>
<td>Cr- -20°C-SmC*- 59°C-SmA</td>
</tr>
<tr>
<td>FLC+0.3% CNT</td>
<td>Cr- -20°C-SmC*- 60°C-SmA</td>
</tr>
<tr>
<td>FLC+0.4% CNT</td>
<td>Cr- -20°C-SmC*- 60.5°C-SmA</td>
</tr>
</tbody>
</table>
A. Pure Mixture

4.3 Dielectric Studies

4.3.1 Frequency Dependence

Frequency dependence of the real and imaginary part of dielectric permittivity ($\varepsilon_\perp'$, $\varepsilon_\perp''$) of FLC-I, in 6 µm cell, at different temperatures is shown in Fig 4.1(a, b) and Fig 4.2(a, b) respectively for the SmC* and SmA phases. It reflects the dielectric spectrum in the form of absorption ($\varepsilon_\perp''$) [Fig 4.1 & 4.2(b)] and dispersion ($\varepsilon_\perp'$) [Fig 4.1 & 4.2(a)] curves. It is seen that $\varepsilon_\perp'$ shows dispersion at a particular frequency. The saturation in the permittivity is observed after this frequency. On the other hand, $\varepsilon_\perp''$ first increases with the increase of frequency attain maxima and then decreases. The position of peak corresponds to the relaxation frequency and occurs at a frequency at which the real part falls to half of its value. This peak in our results corresponds to the relaxation frequency of $GM$ ($f_{GM}$) below transition. The position of peak with respect to the frequency axis shows an increase with temperature near the transition to the SmA phase and is the relaxation frequency of $SM$. The $GM$ dielectric spectrum lies in the frequency range up to 10kHz. The $f_{GM}$ ≈ 2kHz at room temperature as calculated from this peak and that of $SM$ is of the order of 100-300 kHz. Fig 4.3 shows a typical relaxation process in the form of Cole-Cole plot at different temperatures.
Fig 4.1: Frequency dependence of a) real and b) imaginary part of permittivity of FLC-I, in 6 µm sample cell, at different values of reduced temperatures (°C) in the SmC* phase
Fig 4.2: Frequency dependence of the c) real and d) imaginary part of dielectric permittivity of FLC-I, in 6µm cell, at different values of reduced temperatures (°C) in the SmA phases.
4.3.2 Temperature Dependence

The temperature dependence of complex permittivity at different frequencies is shown in Fig 4.4(a, b). The Eq 2.26 gives the contribution of the various relaxation modes to the complex dielectric permittivity. Fig 4.4(a, b) shows a hump near the transition temperature before a sharp decrease. However far below the transition temperature the permittivity shows a saturated value. It is due to the decrease in contribution of $GM$ with the increase of temperature and finally at the transition temperature the $GM$ vanishes following very low permittivity. However a hump is observed just below the transition temperature due to the significant contribution of two modes i.e. $SM$ and $GM$. As seen in Fig.4.2–Fig.4.4, there is a pronounced dispersion region below 2kHz connected with the $GM$ in the SmC* phase. However, near $T_{C^*A}$, a new relaxation region shows up, but its dispersion takes place at much higher frequencies (between 50kHz and 1MHz) in comparison to $GM$. This pretransitional relaxation mode is defined as $SM$, which appears due to the amplitude fluctuations of tilt angle.

Fig.4.3 and 4.5 reflects the $GM$ and $SM$ near $T_{C^*A}$ and SmA phase in the form of Cole-Cole plot. It is seen from Fig.4.5, that only $GM$ appears at lower temperatures, whereas at $T_{C^*A}$ and in the SmA phase only $SM$ appears as can be seen from Fig.4.4.
Fig 4.4: - Temperature dependence of the real and imaginary part of dielectric permittivity (ε′, ε″) of FLC-I, in 6µm cell, at different Frequencies
4.3.3 Dielectric Strength

Dielectric strength is the maximum capacity of a capacitor to store the charge and is related to the dielectric susceptibility as \( \chi = \varepsilon_a \Delta \varepsilon \). The dielectric strength has been calculated using Eq. (2.9). Fig. 4.6 shows the temperature dependence of the dielectric strength \( \Delta \varepsilon_{\perp} \) of GM (calculated in case of 6 µm cell) and SM in the absence of an external bias in SmC* and SmA phase of FLC-I. It is observed that the GM dielectric strength \( \Delta \varepsilon_{GM} \) in the SmC* phase remains almost constant with temperature and then decreases sharply at the transition after showing a hump near the transition temperature. This behaviour of \( \Delta \varepsilon_{\perp} \) can be explained on the basis of the following relation

\[
\Delta \varepsilon_{\perp} = \frac{1}{K} \left( \frac{pP}{\theta} \right)^2
\]

where \( p \) is pitch, \( P \) is the polarization, \( K \) is twists elastic constant and \( \theta \) is the tilt angle. Below \( T_C \) an increase of polarization-tilt ratio and increasing pitch causes the strong increase of dielectric strength. Far from the transition this ratio is almost

![Fig 4.5: Cole–Cole plots at different values of reduced temperature (°C) near and after the transition to SmA* phases](image)
constant and small decrease is due to the decrease of pitch. The twist elastic constant is almost independent of temperature.

Near $T_{C^*A}$, $SM$ starts appearing which shows the characteristic V-shape of dielectric strength in the vicinity of $T_{C^*A}$ as described by mean field model and Curie-Weiss law $f_{SM} = a' + b'(T - T_{C^*A})$, where $a'$ and $b'$ are constants.

![Temperature dependence of Dielectric strength of the GM and SM](image)

**Fig 4.6:** Temperature dependence of Dielectric strength of the GM and SM

### 4.3.4 Relaxation Frequency

Relaxation frequency has been calculated by fitting the experimental data points plot of $\log_{10}(V/U)$ *versus* $\log_{10}f$, which gives a straight line as shown in Fig. 4.7. The intercept on the abscissa corresponds to relaxation frequency $f_r$, and the slope gives the distribution parameter ($\alpha$). The data points deviate from straight line because at low frequencies the value of $(V/U)$ is very small, though $V$ is small but at higher frequencies $V/U$ is very large since $U$ is small. The values of $V$ and $U$ have been calculated by using the Eqn. 3.8(a) and 3.8(b). The temperature dependence of relaxation frequency of $GM$ ($f_{rGM}$) and $SM$ ($f_{rSM}$) in 6µm is shown in Fig.4.8. These values of $f_r$ corresponds to the values found from the peak of $\varepsilon''_\perp$ [Fig.4.2(b)]. It is observed that $f_{rGM}$ in SmC* phase remains almost constant below $T_{C^*A}$ after which
*SM* starts appearing. The temperature dependence of relaxation frequencies follows an Arrhenius type of behaviour.

Fig 4.7: Plot between frequency vs log(V/U)

Fig 4.8: Temperature dependence of Relaxation frequency of the GM and SM
4.3.5 Cell Thickness Dependence

Fig. 4.9 shows the dielectric permittivity ($\varepsilon_\perp'$, $\varepsilon_\perp''$) of FLC-I confined in cells of thickness 3µm, 7.5µm, 25µm and 62.5µm. The cell thickness dependence of permittivity in the form of Cole-Cole plot is shown in Fig. 4.10.

**Fig 4.9:** Frequency dependence of the a) real and b) imaginary part of dielectric permittivity ($\varepsilon_\perp'$, $\varepsilon_\perp''$) of FLC-I, in the cells of different thicknesses (µm)
The magnitude of $\varepsilon_{\perp}'$ in the SmC* phase measured above 2 kHz was almost the same for all these thicknesses but below this frequency a small difference is observed. The permittivity increases with the cell thickness. It can be explained on the basis that the decreases of thicknesses suppress the GM due to increased surface interactions and the contribution of this mode to the permittivity decreases. It also explains the difference in permittivity for various thicknesses only below a frequency of 2 kHz. The detailed explanation however is given in case of electrical parameters section 4.4.1.3 (i).

**4.3.6 Bias Dependence**

The dielectric permittivity in the SmC* phase due to the GM contribution is so high that it becomes difficult to detect the other collective dielectric processes. However, this problem can be overcome by applying bias field, strong enough to unwind the helicoidal structure and suppress the GM. In this way, other collective mechanism can be studied.

![Cole-Cole plots of FLC-I, in the cells of different thicknesses (µm)](image)
The effect of bias on the complex permittivity is shown in Fig. 4.11 for real and imaginary part of permittivity in 6 µm cell. The bias dependence in terms of Cole-Cole plots is also represented in the Fig. 4.12. It is observed that at very low field,
there is negligible effect on the permittivity whereas with increase of field, the permittivity starts decreasing non-linearly. A sharp decrease is observed near the critical field and then at the critical field the magnitude of permittivity falls to very small value. A model representing the effect of field on the sample is shown in Fig 4.13. It is observed with increase of field, helix deforms continuously and then at some value of field the internal disclinations lines becomes the surface disclinations which bifurcate and move in the opposite direction. On further increasing the field a uniform structure appears at some places while in other places the sample is still chiral. Then finally at critical field the whole structure becomes uniform and the complete unwinding of the helix takes place which in turn suppresses the GM and hence decreases the permittivity sharply.

However, it is observed that still there remains the residual part of GM, which cannot be completely suppressed. We may define that residual part of the GM is due to DM and SM.

$$\chi = \chi_{DM} + \chi_{SM},$$

$\chi_{DM}$, $\chi_{SM}$ are the DM and SM susceptibilities respectively.
DM could have appeared due to the formation of domains with different periodicities in the layer structures in presence of an electric field.

![Diagram of domain structures](image)

**Fig 4.13:** A model is representing the effect of field on the sample.

Temperature dependence of the complex permittivity also shows similar effect of bias as shown in Fig 4.14 for real part of permittivity. The variation of dielectric strength and relaxation frequency with bias is shown in the Fig 4.15(a) and Fig 4.15(b). It is observed that the dielectric strength decreases whereas the relaxation frequency increases with bias due to the suppression of $GM$. 
Fig 4.14: Temperature dependence of the dielectric permittivity of FLC-I, at different Bias Voltages.

Fig 4.15(a): Bias Dependence of dielectric strength of FLC-I.
Fig 4.15(b):- Bias Dependence of relaxation frequency of FLC-I
4.4 Electrical Studies

The current reversal method has been used to measure the various electro-optic parameters of dielectric materials as discussed earlier. Here the output may be taken across a capacitor or resistor corresponding to capacitor or resistor methods.

4.4.1 Spontaneous Polarization

Spontaneous polarization measurements have been performed by using capacitor and resistor method. The theory of these methods is discussed in section 2. As discussed earlier, every reorienting dipole imparts a charge impulse and contributes to the polarizing reversal peak in RM. The hump appears near the threshold point of helices winding and unwinding. In CM, the smooth growth of the curve corresponds to the integration of the repolarization current.

In RM, a triangular wave of $2V/\mu m$ and in CM, a square wave of $2V/\mu m$ was applied to the liquid crystal sample. Since the pitch of the material is very small as compared to the sample thickness and surface interaction are kept weak, a deformed helix ferroelectric mode is present in the mixture. So the helix is present in the bulk sample and application of small field results in the deformation of the helix till a critical value of field where the unwinding of the helix takes place and material shows meta-stability. This critical field for DHF structure is

$$E_c = \frac{\pi^2 Kq_0^2}{16 P_s}$$  \hspace{1cm} (4.1)

On changing the sign of the voltage, the polarization state changes giving rise to another state. In this way we can observe up and down polarization states. This dipole orientation results in the polarization hump in RM that directly gives a measure of polarization.

4.4.1.1 Temperature Dependence

The temperature dependence of polarization in cells of thicknesses 6 $\mu$m and 7.5 $\mu$m is depicted in Fig. 4.16(a, b) for CM and RM respectively. It shows that the polarization decreases with increasing temperature and obey the power law as given in eqn.4.2.

$$P_s = A (T-T_{c+})^\beta$$  \hspace{1cm} (4.2)
Fig. 4.16: Temperature dependence of polarization in cells of thickness 6µm and 7.5 µm is depicted in a) for CM and b) for RM respectively.

The critical exponent \( \beta \) as obtained from the theoretical fit is found to be 0.463. A slight change from the theoretical value of 0.5 may be due to the error in measurements, field induced terms (Bresnev et. al. 1988, Miyata et. al. 1996, Srivastava et. al 1993, Wrobel et. al 1995) and experimental conditions.
4.4.1.2 Bias Dependence

Fig. 4.17(a-e) shows the evolution of polarization with bias in the form of oscilloscope traces. It is observed that at very low bias there was polarization peak corresponding to the surface switching only. As the field increases a second hump arises corresponding to the bulk switching. On further increasing the field, bulk

---

**Fig. 4.17:** Variation of Polarization at a) 7V b) 10V c) 15V d) 20V and e) 30V bias voltages.
switching become dominant and finally at the field greater than the critical field required to unwind the helix only single hump exist corresponding to the reorientation between up or down states. The magnitude of polarization as calculated from these traces is shown in Fig. 4.18, which shows that at first the polarization increases with bias and then saturates above the critical field. However the increase is nonlinear with field.

4.4.1.3 Thickness dependence

Now we will discuss the thickness dependence of the spontaneous polarization.

---

**Fig 4.18:** magnitude of polarization as a function of bias voltage for cell of thicknesses 6 µm and 7.5 µm

**Fig 4.19:** Spontaneous polarization as a function of cell thickness
Fig 4.20: Spontaneous polarization as a function of cell thickness

Fig 4.21: Critical Index as a function of cell thickness
The behavior of polarization for sample cells of different thicknesses is shown in Figure 4.19 and Figure 4.20. As expected theoretically, temperature dependence in Figure 4.19 is observed to follow the power law given by

\[ P_s = A (T - T_{C^*})^\beta \]  

(4.2)

Though, \( P_s \) is observed to follow the power law in each case, an increase in its magnitude is observed with the increasing thickness of cell [Figure 4.20]. The critical exponent (\( \beta \)), as obtained from theoretical fit, is given in Figure 4.21 for different cell thicknesses. The index \( \beta \) is almost constant except for 3 \( \mu \)m cell. The small deviation from the theoretical value of 0.5 in each case is due to the field induced terms (Bresnev et al. 1988, Miyata et al. 1996, S. L. Srivastava 1993, Wrobel et al. 1995). The cell thickness dependence of \( T_{C^*} \) (SmC*-SmA* transition temperature) for FLC as obtained from the curve fitting of Figure 4.19, is shown in Figure 4.22. \( T_{C^*} \) tends to decrease with the decrease of cell thickness. However an exception is observed for the case of 3 \( \mu \)m cell where an unusual increase in \( T_{C^*} \) is observed. Here a shift of \( \sim 6 \) °C is observed. A trace of the switching current after passing through transition temperature, as seen in the specimen with cell thickness 3 \( \mu \)m, may be due to smearing out of \( T_c \) because of Electroclinic (EC) effect that comes in to play above a critical value of the biasing field. The increasing value of

Fig 4.22: Transition temperature as a function of cell thickness
P_s and T_{C*} with cell thickness and anomalous behavior in 3 \mu m thick sample are explained in terms of mathematical models given below.

i) Cell thickness dependence

The decrease in P_s and T_{C*} with diminishing cell thickness can be explained in terms of generalized Landau expansion of free energy density (Khoo et. al. (1993), Carlsson et. al 1990 & 1988, Levestik et. al 1987, Fillipic et. al 1988). For a non-chiral system, at any temperature T, free energy density is given by

\[ F = F_0 + \frac{1}{2}a \theta^2 + \frac{1}{4}b \theta^4 + \frac{1}{6}c \theta^6 \]  

(4.3)

Where \( \theta \) is the tilt angle and is the primary order parameter for SmC-SmA transition. \( a=\alpha (T-T_C) \) is only temperature dependent term. \( \alpha, b \) and \( c \) are positive constants for the case of second order transition. The values of these constants are very small near the transition temperature. \( T_C \) is the transition temperature from SmC-SmA phase and \( F_0 \) is the singular part of \( F \).

Now the expression of free energy in the case of an unwound system (for which wave vector \( q=0 \)) for SmC* -SmA* transition is given by (Khoo et. al. (1993), Carlsson et. al 1990 & 1988, Levestik et. al 1987, Fillipic et. al 1988).

\[ F^*(\theta, E) = F_0 + \frac{1}{2}a \theta^2 + \frac{1}{4}b \theta^4 + \frac{1}{6}c \theta^6 + \frac{1}{2}\lambda_0 P^2 - \frac{1}{2}\Omega P^2 \theta^2 + \frac{1}{4}\eta P^4 - EP \]  

(4.4)

Chiral interactions are introduced in the equation by term \( P^2/2\lambda_0 \), here \( \chi_0 \) is the high frequency dielectric constant which is due to the effect of dipolar ordering. \( C \) is piezoelectric bilinear coupling term, \( \Omega \) is biquadratic coupling term and \( \eta \) (a constant) term has been added to stabilize the system. The last term is included to represent the decrease in energy on application of field.

Now minimizing Equation (4.4) with respect to \( P \)

\[ \frac{\partial F^*}{\partial P} = 0 \]

It gives

\[ \left( \frac{1}{\chi_0} - \Omega \theta^2 \right) P - C \theta + \eta P^3 - E = 0 \]
Recently Gouda et al [1994] have pointed out that $\eta$ term is related to low temperature saturation of polarization and is therefore irrelevant near the transition temperature. So, at higher temperatures, we get

$$\left(\frac{1}{\chi_0} - \Omega\theta^2\right)P - C\theta = E \quad (4.5)$$

From Equation (4.5) we have

$$P = \frac{(E + C\theta)}{\left(\frac{1}{\chi_0} - \Omega\theta^2\right)} = \chi_0(E + C\theta)(1 - \chi_0\Omega\theta^2)^{-1} \quad (4.6)$$

In case of second order transition, tilt angle approaches zero continuously at the transition temperature and Equation (4.6) reduces to the form $P=E\chi_0$.

Now, applying condition \( \frac{\partial F^*}{\partial \theta} = 0 \)

\[ a\theta + b\theta^3 + c\theta^3 - CP - \Omega P^2\theta = 0 \]

Substituting $P$ from Equation (4.6), neglecting contribution from higher powers of $\theta$, we get (Lagerwall et. al. 1999)

$$\left(a - C^2\chi_0 - E^2\Omega\chi_0^2\right)\theta - C\chi_0 = 0 \quad (4.7)$$

considering first term in Equation (4.7) (Lagerwall et. al. 1999)

\[
\left(a - C^2\chi_0 - E^2\Omega\chi_0^2\right)\theta = a^* = \alpha(T - T_c) - C^2\chi_0 - E^2\Omega\chi_0^2
\]

\[
= \alpha \left(T - T_c - \frac{C^2\chi_0}{\alpha} - \frac{E^2\Omega\chi_0^2}{\alpha}\right)\theta
\]

$$a^* = \alpha(T - T_c)\theta \quad (4.8)$$

Now $a^* = \alpha(T-T_c^*)$ is temperature dependent term where $T_c^*$ is the SmC*-SmA* phase transition temperature and is given by

$$T_c^* = T_c + \frac{C^2\chi_0}{\alpha} + \frac{E^2\Omega\chi_0^2}{\alpha}$$

Using Equation (4.6) at transition

$$T_c^* = T_c + \frac{C^2\chi_0}{\alpha} + \frac{P^2\Omega}{\alpha} \quad (4.9)$$

Mean field coefficients $C, \alpha, \chi_0, \Omega$ have been found to be positive (Giesselmann et al 1995). Since the last two terms are always positive in Equation (4.9), the
temperature $T_C$ always increases. Also except polarization, all other terms in Equation (4.9) are nearly constant for a particular FLC compound and hence the transition temperature ($T_{C*}$) reaches a maximum value when $P$ becomes $P_{\text{max}}$. So Equation (4.9) can be written as

$$T_{C_{\text{max}}} = T_c + \frac{C^2X_0}{\alpha} + \left(\frac{P_{\text{max}}}{\alpha}\right)^2 \frac{\Omega}{\alpha}$$  \hspace{1cm} (4.10)

Where $P_{\text{max}}$ and $T_{C_{\text{max}}}$ are maximum value of polarization and transition temperature respectively. Now, the critical temperature for FLC can also be written as [Pikin et al (1981)]

$$T_{C*} = T_{C_{\text{max}}} - \left(\frac{\Pi^2 g}{2\alpha}\right) \frac{1}{\left(d + \frac{2g}{|W|}\right)^2}$$  \hspace{1cm} (4.11)

Where $T_{C_{\text{max}}}$ is maximum critical temperature when thickness $d \rightarrow \infty$, $g$ is elastic modulus and $W$ is the effective anchoring energy. From Equation (4.9) and (4.10) we have

$$T_{C*} = T_{C_{\text{max}}} + \frac{\Omega}{\alpha} \left(\frac{P^2}{\alpha} - \frac{P_{\text{max}}^2}{\alpha}\right)$$  \hspace{1cm} (4.12)

On comparing Equations (4.11) and (4.12) we get

$$P = \left[P_{\text{max}}^2 - \left(\frac{\Pi^2 g}{2\alpha}\right) \frac{1}{\left(d + \frac{2g}{|W|}\right)^2}\right]^{1/2}$$  \hspace{1cm} (4.13)

Hence from Equation (4.13), it is clear that as $d \rightarrow \infty$, $P \rightarrow P_{\text{max}}$ i.e. spontaneous polarization increases with cell thickness. Also when $d \left| W \right| >> g$ we have
Equation (4.14) also shows that polarization increases with cell thickness. At \( d \ll W \) the dependence of \( P(d) \) on cell thickness is very small. Equation (4.9) or (4.11) or (4.12) conforms to an increase in transition temperature with cell thickness as observed in Fig. 3 and Fig. 4.

**ii) Anomalous behaviour**

The anomaly in the case of 3 \( \mu \)m sample which shows an abnormal jump in its transition temperature can be explained in terms of EC effect. In 1975 Meyer et al showed that in SmC* phase each layer exhibit \( P_s \) due to chiral nature of molecules. The other consequence of chirality is the helical superstructure due to precession of director around the layer normal. Application of electric field of sufficient strength unwinds the helix of SmC* phase producing homogeneous tilt and hence a net polarization current. This coupling between tilt and polarization can induce itself in SmA* phase, for field above a critical value, and the effect is called EC effect. The director in SmA* phase, usually parallel to layer normal, become tilted at some angles. So, the SmC* and SmA* phase shows same homogeneous tilt i.e. unwound SmC* and SmA* phase have identical symmetry [Garoff \( et \) al (1979)]. The phase transition from SmC* to SmA* phase which is generally second order, become less abrupt. The transition temperature, now, is difficult to analyze and is appeared to show an increase in its value.

The transition from SmC* to the SmA*, in our 3\( \mu \)m cell, found to be less abrupt and conforms to induction of tilt angle in SmA* phase. We were able to observe EC effect in this sample only as in thin samples the field required to attain EC effect is less.

The EC behavior viz. critical field required, shift in transition temperature etc. can be interpreted in term of a simple Landau model. The Landau free energy density is given by Equation (4.4)

\[
F^* (\theta, E) = F_0 + \frac{1}{2} a \theta^2 + \frac{1}{4} b \theta^4 + \frac{1}{6} c \theta^6 + \frac{1}{2} \kappa_0 P^2 - CP \theta - EP
\]

where we have neglected the contribution from biquadratic term as EC effect.
depends strongly on bilinear coupling. In order to calculate the value of critical field required to observe EC effect, we apply condition

$$\frac{\partial F^*}{\partial \theta} = 0$$

The equation for electric field, in terms of tilt angle obtained is:

$$E = \frac{1}{C\chi_o} \left\{ \alpha(T - T_c) - C^2 \chi_o \theta + b \theta^3 + c \theta^5 \right\}$$  \hspace{1cm} (4.15)

At the critical field the following conditions must be satisfied [Bahr et al (1990)]

$$\frac{\partial E}{\partial \theta} = 0, \quad \frac{\partial^2 E}{\partial \theta^2} = 0$$

Using these conditions we get

$$T_{c^*} = T_c + \frac{9b^2}{20\alpha c} + \frac{C^2 \chi_o}{\alpha}$$ \hspace{1cm} (4.16)

$$E_{c^*} = \frac{1}{C\chi_o} \left[ \frac{6\sqrt{3}}{25\sqrt{10}} \left( -b \right)^{5/2} \right]$$ \hspace{1cm} (4.17)

Where $T_{c^*}$ is the transition temperature when field is above a critical value. Now the transition temperature at zero field, after neglecting biquadratic term is [Bahr et al (1990)]:

$$T_{c^*} = T_c + \frac{3b^2}{16\alpha c} + \frac{C^2 \chi_o}{\alpha}$$ \hspace{1cm} (4.18)

The difference in the transition temperature for zero field Equation (4.18) and critical temperature Equation (4.16) or the change in transition temperature $T_{c^*}$ due to EC effect is given by

$$T_{c^*} - T_{c^*} = \frac{21b^2}{80\alpha c}$$ \hspace{1cm} (4.19)

Since $\alpha$, $b$, $c$ are different for different FLC, the increase in $T_{c^*}$ due to EC effect is also different. However, based on the order of each constant the transition temperature can vary up to few K as observed in Figure 4.19 and Figure 4.22.

Now the Equation (4.16) can be modified by use of Equation (4.9) (neglecting biquadratic term)

$$T_{c^*} = T_c + \frac{9b^2}{20\alpha c}$$

So, the critical field equation becomes

$$E_{c^*} = \frac{1}{C\chi_o} \left\{ \alpha \left( T_{c^*} - T_c + \frac{9b^2}{20\alpha c} \right) - C^2 \chi_o \theta + b \theta^3 + c \theta^5 \right\}$$ \hspace{1cm} (4.20)
As discussed in previous section and proved by Pikin et al [1981] $T_{C*}$ decreases with diminishing cell thickness. As a result the value of critical field requirement to attain electroclinic effect is comparatively low in thin samples for a given material. This is the reason behind presence of EC effect in thin samples.

### 4.4.2 Response Time

A symmetric square wave sufficient to unwind the helix was applied to the sample in case of both CM and RM. In RM the polarization peak appears far away from the edge of the input square wave pulse and this delay corresponds to the response time of the material. In CM the slope of polarization section gives a measure of rise time.

#### 4.4.2.1 Temperature Dependence

The temperature dependence of $\tau$ in cells of thickness 6 $\mu$m and 7.5 $\mu$m is depicted in Fig. 4.23(a,b) for CM and RM respectively. It is observed that the temperature dependence of $\tau$ obeys the same trend as given by an Arrhenius law. The area under the polarization hump decreases with temperature and the response of the material to the applied pulse become sharp resulting in a faster response. It is observed that the switching is faster in the region of electroclinic effects.

![Graph showing temperature dependence of response time](image-url)

(a)

179
4.4.2.2 Bias dependence

The variation of \( \tau \) with bias is reflected in Fig. 4.24. It is observed that at very low bias i.e. well below the critical field there was a strong decrease in the response time and is found to vary inversely with field. On further increasing the field, above the critical limit the \( \tau \) saturates and the same has been predicted by S. L. Srivastava [1993]. The response time is found to be inversely proportional to the square root of field.
Thickness dependence of $\tau$ is shown in Fig. 4.25. It is found to be strongly dependent on thickness of the sample and varies directly with thickness. The response of the mixture changes from almost 200$\mu$sec to 3msec as the thickness changes from 6$\mu$m to 25$\mu$m. It is due to increased surface force on decreasing the thickness of the sample. The increasing effect of surface suppresses the helix and it helps in
switching. The increased viscosity of the sample is also responsible for the slower response of the material.

4.4.3 Rotational Viscosity

4.4.3.1 Temperature Dependence
The rotational viscosity is obtained from the product of spontaneous polarization and response time of the liquid crystals mixture. The temperature dependence of the rotational viscosity is shown in the Fig. 4.26. It follows the same Arrhenius law as predicted by theory. The viscosity of the material decreases with temperature and this decreasing value of viscosity is also a reason for faster response of the material near the transition temperature.

4.4.3.2 Thickness dependence
Variation of rotational viscosity for the cells of different thickness is shown in the Fig. 4.27. It is observed to increase with the increasing thickness and hence results in the slower response of the mixture.

4.4.4 Activation Energy
The activation energy of the material can be obtained by fitting the Arrhenius law to the rotational viscosity vs temperature curve. Activation energy of the material in the SmC* phase comes out to be 0.34eV. Same value is also obtained by fitting the curve from the variation of relaxation frequency with temperature. However, the temperature dependence of the activation energy can be calculated at a particular frequency by using the equation

\[ E_u = RT \left[ 22.92 + \ln \left( \frac{T}{f} \right) \right] \]  

(4.21)

where R is a gas constant, T is the temperature and f is the relaxation frequency in case of FLCs. The temperature dependence of activation energy can be predicted from this equation.
Fig 4.26: Rotational viscosity as a function of reduced temperature for 6 µm

Fig 4.27: Rotational viscosity as a function of reduced temperature at different cell thicknesses (µm)
4.4.5 Azimuthal Angle

The variation of azimuthal angle as a function of temperature for FLC material as measured with the help of capacitor method is shown in Fig. 4.28. It is found to remain almost constant in the SmC* phase and finally increases sharply after a decrease near the phase transition temperature.

Since the azimuthal angle is related to the wave vector by relation $\phi_0 = qz$, it follows the trend similar to wave vector. According to the theoretical predictions the variation of wave vector of pitch with temperature follows the equation (Khoo et. al. 1993, Carlsoon et. al. 1990 & 1988, Levestik et. al 1987, Fillipic et. al 1988)

$$q = \frac{\lambda}{k_3} + \frac{\mu P_{\alpha}}{k_3 \theta_\alpha} + \frac{d\theta_\alpha^2}{k_3} \tag{4.22}$$

Where ‘q’ is a wave vector of the pitch, $K_3$ elastic modulus, $\mu, \lambda$ are coefficients of Lifshitz term responsible for flexo-electric bilinear coupling. At low temperature, it slowly decreases with rise in temperature, reaches a minimum value and then finally rises to a finite value at the transition temperature. Our experimental results for temperature dependence of azimuthal angle, as in Fig 4.28, show the same behavior as depicted by the theoretical curve for q (Carlsoon et. al. 1990 & 1988, Levestik et. al 1987, Fillipic et. al 1988).

Fig 4.28: Azimuthal angle as a function of reduced temperature at different cell thicknesses (μm)
B. Guest-Host Mixture

4.5. Dielectric studies

4.5.1 Frequency Dependence

The guest-host mixtures of FLC-I have been prepared with 0.1%, 0.2% and 0.4% wt/wt concentration of MWCNTs. The effect of CNTs on the complex permittivity is reflected in terms of its frequency dependence in SmC* and SmA phases, as shown in Fig. 4.29(a, b) and Fig. 4.29(c, d) respectively. The relaxation of a mode at a particular frequency follow-on to the dispersion of $\varepsilon'$ whereas a peak is observed in the $\varepsilon''$. This frequency corresponds to the relaxation frequency of the mode. Fig. 4.29 shows the presence of two relaxation modes at lower (Goldstone mode) and higher frequencies (Soft mode) respectively in all the mixtures. These are due to the collective motions of the molecules in the liquid crystalline phase. These relaxation modes are reflected in Fig 4.30 in the form of Cole-Cole plots at different temperatures. It is seen that the GM is dominant only in the SmC* phase and its contribution decreases at higher temperature due to the unwinding of helix. Since, at $T_{C^*A}$ (transition temperature from SmC* to SmA phase), the permittivity has contribution only from the SM, it shows a sahrp decreases in its magnitude.

The comparison of pure and dyed mixtures shows a decrease in real ($\varepsilon'$) and imaginary ($\varepsilon''$) part of permittivity with increase in CNTs concentration in the SmC* phase but an increase in permittivity is observed in the SmA phase. It was seen that effect of CNTs is almost negligible up to 0.1% concentration and a noticeable effect is observed only when the CNTs concentration is increased to 0.2%. The effect is also represented in the form of Cole-Cole plots [Fig 4.30(a)].

Fig. 4.31 and 4.32 presents the variation of the real ($\varepsilon'$) and imaginary ($\varepsilon''$) part of the permittivity at different values of reduced temperature ($\Delta T = T - T_{C^*A}$, where $T_{C^*A}$ is the temperature of the SmC*-SmA phase transition) in the pure and 0.2 % CNTs doped materials. We notice an overall decrease in permittivity in the SmC* phase with addition of CNTs (Figure 4.31), whereas it increases in the SmA* phase (Figure 4.32). It is also represented by the Cole-Cole plots as shown in Fig 4.33. A comparison between $\varepsilon'$ values in Figure 4.31(a) and 4.32(a) reveals that $\varepsilon'$ in SmC*
phase is about 20 times greater than the $\varepsilon'$ in SmA* phase for pure mixture but this difference narrows down to about 6 times for 0.2 wt% CNTs addition.

Fig 4.29: Frequency dependence of the a) real and b) imaginary part of dielectric permittivity ($\varepsilon_\perp'$, $\varepsilon_\perp''$) of pure FLC-I and its guest-host mixtures in SmC* phase.
Fig 4.29: Frequency dependence of the c) real and d) imaginary part of dielectric permittivity ($\varepsilon_\perp^\prime$, $\varepsilon_\perp^\prime\prime$) of pure FLC-I and its guest-host mixtures in SmA* phase.
Fig 4.30: Cole-Cole plots of pure FLC-I and its guest-host mixtures in the (a) SmC* and (b) SmA phase
Fig 4.31(a, b): Frequency dependence of the real and imaginary part of dielectric permittivity ($\varepsilon_\perp''$, $\varepsilon_\perp''$) of pure FLC-I and its 0.2% CNTs doped mixture at different temperatures in SmC* Phase.
Fig 4.32(a, b):- Frequency dependence of the real and imaginary part of dielectric permittivity ($\varepsilon_\perp'$, $\varepsilon_\perp''$) of pure FLC-I and its 0.2% CNTs doped mixture at different temperatures in SmA* phase
4.5.2 Temperature Dependence

The temperature dependence of all these mixtures shows a dispersion in permittivity to a very small value in SmA phase after giving a hump near the transition temperature, Fig 4.34(a, b). However, far below the transition temperature magnitude of complex permittivity shows a saturated value. We notice an overall decrease in permittivity in the SmC* phase with addition of CNTs (Figure 1), whereas it increases in the SmA* phase (Figure 4.34). These experimental results indicate that the permittivity shows an opposite effect in SmC* than in SmA phase on CNTs addition in ferroelectric liquid crystal possessing deformed helix ferroelectric structure.

4.5.3 Dielectric Strength and Relaxation Frequency

The temperature dependence of the dielectric strength ($\Delta \varepsilon_G$) of the GM, as shown in Figure 4.35, shows a decrease in SmC* phase with slight inversion of effect near $T_{C^*}$ on CNTs addition. The dielectric strength ($\Delta \varepsilon_S$) of SM (SmA* phase), on the other hand, increases for the nano-composite. The temperature dependence of the relaxation frequency for GM ($f_G$) and SM ($f_S$) is shown in Figure 4.36. The relaxation frequencies of the GM does not show any significant change in its value on CNTs addition, whereas a decrease is observed for SM in the SmA* phase.

Fig. 4.33: Cole-Cole plots in the (a) SmC* and (b) SmA phase at different values of reduced temperature (°C) for Pure and 0.2% CNTs doped Sample

191
Fig 4.34: Temperature dependence of a) real and b) imaginary part of dielectric permittivity of Pure and guest host derivatives of FLC.
Fig 4.35: Temperature dependence of dielectric strength of Pure and guest host derivatives of FLC-

Fig 4.36: Temperature dependence of relaxation frequency of Pure and guest host derivatives of FLC-

193
4.5.4 Theoretical Explanation

These variations are attributed to the change of elastic constant and effect on DHFLC molecular packing, on CNTs inclusion. Before going into detail of these considerations, we discuss the structure of SmC* and SmA* phases and the equations for dielectric parameters of their relaxation modes.

The SmC* structure, in the relaxed state, is helicoidal and can be represented in terms of a one-dimensional model giving the azimuthal angle $\phi$, as a function of $z$ along the helical axis, $\phi = qZ$ where $q = 2\pi/p$ is the wave vector of the helix pitch ‘$p$’.

The ordering of the molecule in this phase is represented by the two order parameters, $\xi$ and $P$ representing the magnitude and direction of tilt angle and the polarization respectively (Musevic et. al. 2000, Blinov et. al. 1994, Wrobel et. al. 1995 Biradar, et. al. 1989, Gathania et. al. 1999).

$$
\xi(Z) = \theta, [\hat{x} \cos \phi + \hat{y} \sin \phi] \\
P(Z) = P, [-\hat{x} \cos \phi + \hat{y} \sin \phi]
$$

(4.22)

If P from Equation (4.22) is projected on a circle as a function of ‘$\phi$’ over a full period, we get isotropic distribution of P that gives no average polarization along y-axis. An application of field in y direction results in anisotropic distribution of P yielding a net $P_y$ component, given by (Wrobel et. al. 1995 Biradar, et. al. 1989, Gathania et. al. 1999, Gauda et. al. 1989).

$$
P = \epsilon_0 (\epsilon_\infty - 1)E + \epsilon_0 \Delta \epsilon G E
$$

(4.23)

It is this component which is the origin of Goldstone mode contribution to the dielectric constant ($\Delta \epsilon G$), the contribution due to linear deformation of helicoidally ordered P Vectors (Gauda et. al. 1989). When the helical structure is deformed and then allowed to relax it returns to the unperturbed state after a relaxation time ‘$\tau_G$’ due to the action of elastic torque and dissipative viscous torque. So, the parameters, elastic constant ($K_\phi$), relaxation time ($\tau_G$), rotational viscosity ($\gamma_\phi$) and dielectric strength ($\Delta \epsilon G$) of Goldstone mode are interrelated. Since far from the transition temperature, GM is the only mode that contribute to dielectric permittivity, the dielectric parameter of GM are used to measure the complex permittivity ($\epsilon^*$) of SmC* phase (Panarin, et. al. 1994, Marzec et. al. 1994). Now, starting from the viscoelastic equation, the relations of $\Delta \epsilon G$, $\epsilon^*$ and $f_G$ (relaxation frequency of GM) are as follows (Blinov et. al. 1994, Gauda et. al. 1989, Panarin, et. al. 1994):
\[ \Delta \varepsilon_G = \frac{p^2}{2\varepsilon_0 K q^2 \theta^2} \quad (4.24) \]
\[ \varepsilon^* = \varepsilon_\infty + \frac{\Delta \varepsilon_G}{1 + (i \omega \tau_G)^{1-a_c}} \quad (4.25) \]
\[ f_G = \frac{p^2}{4 \pi \gamma G \Delta \varepsilon_G \theta^2} \quad (4.26) \]

Where \( a_c \) is distribution parameter and is zero for Debye type behaviour that constitute single relaxation mode. These relations are also obtainable from generalized Landau Model (Zeks et al. 1988, Carlsson, et al. 1990, 1988 & 1987). In SmA* phase, however, the Phasons are degenerate and contribution from the GM vanishes. Only amplitude fluctuations are present. The mode associated with these fluctuations is termed as soft mode and appear in the vicinity of \( T_C \) and up to few degree above in the SmA* phase. Equation (4.25) can also be used to calculate complex permittivity of SM. The dielectric strength, distribution parameter and relaxation time of GM, however, are replaced by that of SM. The fit of Equation (4.25) for zero value of distribution parameter to complex permittivity of pure and CNT doped FLC mixtures, at temperatures well in the SmC* [-25 °C, Figure 4.31] and SmA* phase [1.0 °C, Figure 4.32 (inset)], is represented by solid lines. The values of dielectric parameters, dielectric strength and relaxation frequency, obtained by theoretical fitting matches with those obtained experimentally. It justifies the presence of single relaxation mode in both phases: GM in SmC* phase and Soft mode in SmA* phase.

Now, first we take the effect of elastic energy on dielectric parameters in CNTs-doped DHFLC material. The elastic modulus of CNTs is much larger than that of LC (Yu et. al. 2000). The strong interaction between CNTs and DHFLC molecules increases the elastic energy of DHFLC molecules and therefore attributed to the increase in elastic constant in the CNT-doped LCs (Jeon et. al. 2007). According to Equation (4.24) and Equation (4.25) it decreases the dielectric strength and permittivity in the SmC* phase.

Next we consider the change in physical parameters due to the intrinsic properties of DHFLC material. It is well known that DHFLC materials are short pitched, highly viscous, tightly packed materials. The doping of CNTs affects the packing of DHFLC and reduces its chiral content. Theoretically dilution of the chiral content increases pitch (Blinov et. al. 1994, Stegemeyer, et. al. 1995, Colling
et. al. 2003) which further reduces the polarization (Blinov et. al. 1994, Stegemeyer, et. al. 1995, Colling et. al. 2003). The decrease in the dielectric constant of Goldstone mode (Figure 4.35) is expected as it depends on the square of polarization which is decreasing [Equation (4.24)]. Using Equation (4.25), we can say that, this further decreases the permittivity of SmC* as is observed in Figure 4.31. The relaxation frequency of GM that depends on the ratio of polarization and dielectric strength, however, does not show much change in its value Figure 4.36. Although, dipole moment of CNT add to polarization and hence permittivity but its effect is less dominant than effect of increased elastic constant and dilution of chiral content.

In SmA* phase, only soft mode contribute to the permittivity. The transition from SmC* to the SmA* phase, in CNT-LC mixture (Figure 4.34), seems to be less abrupt increasing the tilt angle variation. The contribution of the soft mode increases simply due to the tilt angle variations. It further increase the complex permittivity of SmA* phase (Figure 4.32) and hence the dielectric strength (Figure 4.35). the effect of dipole moment also adds to permittivity.

The ionic conductivity is calculated from the loss curve. It comes out to be of the order of 10^{-7} \, \text{S/m} for pure (4.71\times10^{-7} \, \text{S/m}) as well as CNT doped (2.8\times10^{-7} \, \text{S/m}) samples at 100 Hz.

### 4.6. Electrical Studies

#### 4.6.1 Spontaneous Polarization

The temperature dependence of the polarization for pure mixtures and its G-H derivative is shown in Fig. 4.37. Both the mixtures show an arrhenius dependence of polarization and fit to the curves gives almost the same value of critical exponent as obtained from the mean field theory. We notice an overall decrease in polarization in the SmC* phase with addition of CNTs (Fig. 4.37), However the effect of CNT appears to reverse near the transition to the SmA* phase (Fig. 4.37). It may due to unwinding of the helix in the SmC* phase on addition of CNTs. The suppression of helix in this case results in decreased value of polarization with CNTs. In the SmA phase the helix is already unwound. However, due to increased viscosity in the CNTs samples, surface anchoring increases and hence the dipole moment of CNTs
also contributes to the polarization. As a result the polarization increases near SmA phase.

![Graph showing variation of spontaneous polarization as a function of reduced temperature for pure and guest host mixtures.](image)

**Fig 4.37:** Variation of spontaneous polarization as a function of reduced temperature for pure and guest host mixtures

### 4.6.2 Response Time

The variation of response time of pure and doped FLCs as a function of reduced temperature ($\Delta T = T - T_{C^*}$, $T_{C^*}$ is transition temperature from SmC*-SmA* phase) is presented in Fig. 4.38. As shown in the Fig 4.38, after doping with CNTs, an improvement (decrease) in response time is obtained in the SmC* phase followed up to the SmA* phase. The reduction of response time of LC makes it suitable for large number of applications. This allows a possible application of CNT doped FLC in the LCD industry.
The temperature dependence of the rotational viscosity, Fig. 4.39, also shows a decrease in SmC* phase on CNTs addition.

**4.6.3 Rotational Viscosity**

The temperature dependence of the rotational viscosity, Fig. 4.39, also shows a decrease in SmC* phase on CNTs addition.

Fig 4.38:- Variation of response time as a function of reduced temperature for pure and guest host mixtures

Fig 4.39:- Variation of Rotational viscosity as a function of reduced temperature for pure and guest host mixtures
4.6.4 Activation Energy

A fit to the rotational viscosity curve gives a measure of activation energy. The $E_a$ for pure material was found to be 0.34ev. It is comparable with the activation energy found in other SmC* compounds [Biradar et al (1996)]. The activation energy of the CNTs doped sample is found to be more than the activation energy of pure sample.

4.6.5 Theoretical Model

These variations in electrical parameters are attributed to the increase of surface anchoring energy and effect on DHFLC molecular packing, on CNTs inclusion. Before going in to detail of these considerations, we discuss the structure of SmC* and SmA* phases and the equations for electrical parameters. The structure of these phases is discussed in equation 4.22 and 4.23. Now, starting from the viscoelastic equation, the relations for $P$, $\tau_G$ and $\gamma_\phi$ are as follows (Blinov et al. 1994, Gauda et al. 1989, Panarin, et al. 1994):

$$q^2 = \frac{P^2}{2\varepsilon_o K_\phi \Delta \varepsilon_o \theta^2}$$  \hspace{1cm} (4.27)

$$\tau_G = \frac{\gamma_\phi}{K_\phi q^2}$$  \hspace{1cm} (4.28)

$$\gamma_\phi = \frac{P^2}{4\pi \varepsilon_o \theta^2 (\Delta \varepsilon_o f_G)}$$  \hspace{1cm} (4.29)

These relations are also obtainable from generalized Landau Model (Zeks et al 1988, Carlsson, et. al. 1990, 1988 & 1987). The equation (4.28), representing relaxation time ($\tau_G$) is, however, valid only up to the field of helix unwinding $E_u$ (Blinov et al. 1994, Beresnev 1989)

$$E_u \approx \frac{K_\phi q^2}{P_s}$$  \hspace{1cm} (4.30)

For $E \geq E_u$, the equation (4.28) reduces to the form (Blinov et al. 1994, Vaksman et al. 1992, Raina et. al. 2000)

$$\tau_S = \frac{\gamma_\phi}{P_s E}$$  \hspace{1cm} (4.31)

Here $\tau_S$ represents the time for switching of the molecule between two polarization states (parallel and anti parallel to the electric field) without the sample going to the helicoidal state. The time interval for this reorientation is called switching time and depends upon the polarization and the rotational viscosity. This equation is used for
the response time measurement of our samples. In SmA* phase, the phasons are degenerate and only amplitude fluctuations are present. In this phase no net polarization exists. However, induction of tilt on applying field may induce electroclinic effect in some cases resulting in some net polarization and very fast switching in SmA* phase.

Now, first we take the effect of doping of CNTs on DHFLC molecular packing. It perturbs the spontaneous polarization (Fig 4.27) and hence response time as well as rotational viscosity. It is well known that DHFLC materials are short pitched, highly viscous, tightly packed materials. The doping of CNTs affects the packing of DHFLC and reduces its chiral content. Theoretically, dilution of the chiral content increases pitch and reduces wave vector (Blinov et. al. 1994, Stegemeyer, et. al. 1995, Collings et. al. 2003). According to equation (4.27) it further reduces the polarization (Blinov et. al. 1994, Stegemeyer, et. al. 1995, Collings et. al. 2003). Now, in the transition from SmC* to the SmA* phase, tilt angle and hence polarization is supposed to be approaching to zero. However, in CNT-LC mixture (Fig 4.37), the transition seems to be less abrupt, thereby inducing the tilt angle variation near the SmA* phase. The contribution near this phase increases simply due to the tilt angle variations. As polarization is considered as the order parameter its decrease in SmC* phase also decreases the rotational viscosity (Equation 4.28) and hence the response time of the materials.

The decrease in rotational viscosity is also attributed to the fact that both CNTs and DHFLC molecules experience a torque due to their nontrivial dielectric anisotropies on the application of electric field and hence the decrease in viscosity has been observed. This also reduces the response time of (Equation 4.30) CNT doped DHFLC material.

Next, we take the effect of anchoring energy that reduces response time in CNTs-doped DHFLC material. It has been observed that CNTs increase the surface anchoring by 1 order (Biradar et. al. 1989). The increase in anchoring energy is due to the π-π electron stacking between CNTs, surface alignment layer, and DHFLC molecules (Lu et. al. 2008, Jeon et. al. 2007, Park et. al. 2007). The relation of response time with the anchoring energy for strong and weak anchoring, respectively, can be expressed as follows (Nie et. al. 2007):

$$
\tau = \frac{v_\phi}{K_\phi \pi^2 \left(d^2 + \frac{4dK_\phi}{W}\right)} \\
(4.32)
$$
where \( d \) is cell gap, and \( W \) is the anchoring energy strength coefficient. Since, cell gap in our case is fixed, so \( d \) will not affect much in above equations. In case of strong anchoring or weak anchoring, the LC response time is inversely proportional to the anchoring energy. The increased anchoring energy lowers the response time in nano-composite. Though the decreased polarization may increase response time as expected from eqn (4.31), the effect of decreased polarization is negligible [Fig. 4.37] as compared to the effect of viscosity [Figure 4.38] and anchoring energy on response time. The eqn 4.31 also shows that decrease of rotational viscosity is one of the reason behind the decrease of response time. The addition of CNT is also seen to improve the alignment of the FLC as shown in Plate 4.1. The improvement of alignment is also a reason for the reduced response time of FLC on CNT addition.

4.7 Comparison of Resistor and Capacitor method

4.7.1 Effect of change in resistance and capacitance

The response time measurements have been carried out using standard resistors (2kΩ-1MΩ) and capacitors (10nF-100nF) in the current reversal technique. The impedance of these electrical elements was smaller than that of the liquid crystals cell. The variation of response time (\( \tau \)) as a function of resistance and capacitance for 5 µm and 25µm thick samples is shown in the Fig. 4.40(a, b) respectively. It is interesting to note that the change in capacitance [Fig. 4.40(b)] has negligible effect on response time whereas it increases with increase in resistance [Fig. 4.40(a)]. The response time also depends on sample thickness. This change is steep in 25µm cell in comparison to the thin cells beyond 20KΩ. The response time is found to be almost constant at lower resistances (<20KΩ to 2KΩ), in both cases. Although more precise measurements can be made with low resistance, but it was difficult to obtain output waveform below 2KΩ. Response time was determined precisely by extrapolating the curve obtained in Fig. 4.40(a). The value thus obtained was approximately the same as in the case of capacitor methods (~200µs, at room temperature).

4.7.2 Effect of Frequency

A typical plot of the frequency dependence of the response time at different resistances is shown in Fig. 4.41. It is observed that increase in frequency has almost negligible effect on ‘\( \tau \)’ until the time period of applied square pulse is greater than the response time of the ferroelectric liquid crystal. So, for a resistance of say 1MΩ, we can use higher working frequency (i.e. >20Hz, used generally), depending upon the response time of the liquid crystal material. It is expected that the range could be
still widened at the lower resistances. This is because ‘τ’ is directly proportional to the external resistance used and thus decreases with resistance. It is also observed that while using the capacitor in the circuit we could use higher frequency as compared to resistance method.

**4.7.3 Effect of Temperature**

The temperature dependence of the response time ‘τ’ for FLC-6304 in 5 µm sample using both methods is shown in Fig.4.42. Although there is a difference in magnitude, It shows an Arrhenius behaviour of the response time dependence on temperature, near the SmC* to SmA transition, for a FLC material.

**4.7.4 Theoretical Models**

**4.7.4.1 Model 1**

The effect of frequency can be explained with the help of relation between time constant of the circuit \((R_cC_c)\) and time period of the input signal \((T)\).

For resistance method (RM), we get desired shape of the output waveform, when

\[
R_cC_c << T \tag{4.34}
\]

whereas, for capacitor method (CM), we get output signal, when

\[
R_cC_c >> T \tag{4.35}
\]

These relations suggest that for CM, the peak will be observed at higher frequencies and the maximum frequency that can be used for the measurement is relatively low in case of RM. The reason for the changing value of response time may also be explained with the help of following relations. The output voltage across the resistor is given by

\[
V_o = \frac{1}{C_c} \int_{0}^{i} idt
\]

\[
V_o = \frac{1}{C_c} \int_{0}^{i} \frac{V_i}{R_c} dt \tag{4.36}
\]

The above equation signifies that if \(R_c\) is large, then current ‘i’ in the circuit become small, so the charging of the capacitor to a required voltage takes longer time. It may also be explained on the basis of the relation (Vaksman et. al. 1992)
\[ Q = C_e V_s \left( 1 - e^{\frac{-t}{RC}} \right) \] (4.37)

where \( Q \) is the charge induced in the circuit on application of field. This equation represents that for large resistance the time constant increases and hence the charging of the capacitors will be delayed resulting in the increase of \( \tau \). This may be the reason for the changing value of response time using resistance. In case, the response time is measured using the external capacitor, the input current is same for both the capacitor and it is decided by the resultant capacitance of the circuit. As the capacitors are connected in series the resultant capacitance will always be close to the smaller one, the LC cell. It is also confirmed by our experimental results, which show that the results of capacitor method are more constant as compared to the resistance method. So we can say that in case of electro-optic methods the switching time measurements using capacitor gives more reliable and accurate determination of response time.

### 4.7.4.2 Model 2

Theoretically we consider that with the resistor method, the voltage generator drives an \([(R_{LCC} / C_{LCC}) \text{ series (R)}] \) equivalent dipole, while with the capacitor method, the voltage generator drives an \([(R_{LCC} / C_{LCC}) \text{ series (C //C_{osc} //R_{osc})}] \) dipole. In the former case the dependency of \( R \) vanishes for \( R_{LCC} >> R \). However a decreasing effect also implies a decreasing signal. So it is not possible to go below a certain value of \( R \) and dependence of response time on \( R \) cannot be removed. This explains the variation of response time with resistance and its comparatively larger value at the higher resistance.

In the latter case while \( C_{osc} \) can be safely neglected (13 pF), \( R_{osc} \) cannot, as it is 1MΩ. However, the effect vanishes for \( C >> C_{LCC} \). While for low \( C \), the case reappears due to \( R_{osc} \), very large value of \( C \) is restricted as it results in vanishing signal. However, it is easy to select a capacitance value that gives the desired output waveform with negligible dependence on \( C \). In our case a negligible effect of \( C \) on response time using capacitance in the range 10-100 nF was observed as shown in Fig 40(b). These theoretical considerations explain the changing value of \( \tau \) with resistance and how this effect can be minimized using universal method.
Plate 4.1: The alignment of the (a) Pure FLC and (b) FLC + CNT
Fig 4.40 (a): variation of response time as a function of resistance

Fig 4.40 (b): variation of response time as a function of capacitance
Fig 4.41: variation of response time as a function of Frequency for different values of resistance

Fig 4.42: variation of response time as a function of temperature for Resistance and capacitor method
Part –2
FLC-II

SCE-8

Geometry
Surface Stabilised Ferroelectric Liquid Crystal mixture

Due to the small sample thickness to helical pitch ratio ($d_S << \rho_0$), and long pitch as compared to the wavelength of light used, we consider that the cell is in the surface stabilised ferroelectric liquid crystal state

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Transitions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure FLC</td>
<td>SmC* - 59°C – SmA - 79°C - N* - 100°C - I</td>
</tr>
<tr>
<td>FLC+0.2% CNT</td>
<td>SmC* - 59°C – SmA - 79°C - N* - 100°C - I</td>
</tr>
</tbody>
</table>
C. Pure Mixture

4.8 Dielectric Studies

4.8.1 Frequency Dependence

Frequency dependence of the real and imaginary part of dielectric permittivity ($\varepsilon_{\perp}'$, $\varepsilon_{\perp}''$) of FLC-II, in 6 µm cell, at different temperatures is shown in Fig 4.43(a, b) and Fig 4.44(a, b) respectively for the SmC* and SmA phases. It reflects the dielectric spectrum in the form of absorption ($\varepsilon''$) [Fig 4.43 & 4.44(b)] and dispersion ($\varepsilon'$) [Fig 4.43 & 4.44(a)] curves. It is seen that $\varepsilon'$ shows dispersion at a particular frequency. The saturation in the permittivity is observed after this frequency. On the other hand, $\varepsilon''$ first increases with the increase of frequency attain maxima and then decreases. The position of peak corresponds to the relaxation frequency and occurs at a frequency at which the real part falls to half of its value. This peak in our results, in SmC* phase, corresponds the relaxation frequency of \( GM \) \( (fr_{GM}) \) below transition. The position of peak with respect to the frequency axis shows a decrease with temperature in the SmA* phase. This might be some new relaxation mode (NRM). The relaxation in SmA* phase at higher frequencies corresponds to \( SM \) which appear due to amplitude fluctuations of tilt angle. The \( GM \) dielectric spectrum lies in the frequency range up to 10kHz. For FLC-II, the \( fr_{GM} \approx 500 \) Hz at room temperature as calculated from the peak and that of \( SM \) seems to be above 10 MHz, beyond the range of the LCR set up. The relaxation frequency of NRM is 50-100Hz. Fig 4.45 shows relaxation processes in the form of Cole-Cole plot at different temperatures.
Fig 4.43: Frequency dependence of a) real and b) imaginary part of permittivity of FLC-II, in 6 µm sample cell, at different values of reduced temperatures (°C) in the SmC* phase.
Fig 4.44:- Frequency dependence of the a) real and b) imaginary part of dielectric permittivity of FLC-II, in 6µm cell, at different values of reduced temperatures (°C) in the SmA phases.
4.8.2 Temperature Dependence

The temperature dependence of complex permittivity at different frequencies is shown in Fig 4.46(a, b). Fig 4.46(a, b) shows a sharp decrease at the transition temperature. However far below the transition temperature the permittivity shows almost a saturated value. It is due to the decreases in contribution of $GM$ with the increase of temperature and finally at the transition temperature the $GM$ vanishes following very low permittivity. However, a hump is observed just below the transition temperature due to the significant contribution of two modes i.e. $SM$ and $GM$. As seen in Fig.4.44–Fig.4.46, there is a pronounced dispersion region below 1 kHZ connected with the $GM$ in the SmC* phase. However, up to a few degree above $T_{C^A}$ in the SmA* phase, a new relaxation region shows up, but its dispersion takes place at 50-100 Hz as is clear from Fig 4.46 (a, b). The relaxation of SM takes place at much higher frequencies (above 10 MHz) in comparison to $GM$. Fig.4.45 reflects the $GM$ and $SM$ in the form of Cole-Cole plot. It is seen from Fig.4.45, that only $GM$ appears at lower temperatures, whereas both GM and $SM$ appears near $T_{C^A}$. In the SmA* phase two mode appear. The one at lower frequency is considered as NRM whereas the other at higher frequencies is considered as $SM$. 

![Fig 4.45: Cole-Cole plots at different temperatures ($^0$C) in the a) SmC* and b) SmA phases](image)
4.8.3 Dielectric Strength

Dielectric strength is the maximum capacity of a capacitor to hold the charge and is related to the dielectric susceptibility as $\chi = \varepsilon_a \Delta \varepsilon$. The dielectric strength has been measured for different frequencies and temperatures, as shown in Fig 4.46.

Fig 4.46: Temperature dependence of the real and imaginary part of dielectric permittivity ($\varepsilon'_\perp$, $\varepsilon''_\perp$) of FLC-II, in 6µm cell, at different Frequencies

4.8.3 Dielectric Strength

Dielectric strength is the maximum capacity of a capacitor to hold the charge and is related to the dielectric susceptibility as $\chi = \varepsilon_a \Delta \varepsilon$. The dielectric strength has been measured for different frequencies and temperatures, as shown in Fig 4.46.
calculated using Eq. (2.9). Fig. 4.47 shows the temperature dependence of the dielectric strength ($\Delta\varepsilon$) of GM (calculated in case of 6 $\mu$m cell) in the absence of an external bias in SmC* phase of FLC-II. It is observed that the GM dielectric strength ($\Delta\varepsilon_{GM}$) in the SmC* phase remains almost constant with temperature and then decreases sharply at the transition after showing a hump near the transition temperature.

This behaviour of $\Delta\varepsilon_\perp$ can be explained on the basis of the following relation

$$\Delta\varepsilon_\perp = \frac{1}{K} \left( \frac{pP}{\theta} \right)^2$$

where $p$ is pitch, $P$ is polarization, $K$ is twist elastic constant and $\theta$ is the tilt angle. Below $T_C$ an increase of polarization-tilt ratio and increasing pitch causes the strong increase of dielectric strength. Far from the transition, this ratio is almost constant and small decrease is due to the decrease of pitch. The twist elastic constant is almost independent of temperature.

Near $T_{C^{\star A}}$, SM starts appearing. The dielectric strength of SM could not be calculated due to the experimental limitations.

![Fig 4.47: Temperature dependence of Dielectric strength of the GM](image-url)
4.8.4 Relaxation Frequency

Relaxation frequency (fr) has been calculated by fitting the experimental data points plot of log10(V/U) versus log10f, as discussed earlier in the section 4.3.4 of this chapter. The temperature dependence of relaxation frequency of GM (fr\textsubscript{GM}) of FLC-II in 6µm is shown in Fig.4.48. These values of fr corresponds to the values found from the peak of $\varepsilon_{\perp''}$ [Fig. 4.43(b)]. It is observed that fr\textsubscript{GM} in SmC* phase remains almost constant below TC*A and then shows a small increase near transition temperature. The temperature dependence of relaxation frequencies follows an Arrhenius type of behaviour. The relaxation frequency of SM was lying beyond the measured range.

4.8.5 Bias Dependence

The effect of bias on the complex permittivity, in 6 µm cell of FLC-II, is shown in Fig. 4.49. The bias dependence in terms of Cole-Cole plots is also represented in Fig. 4.50. It is observed that there is negligible effect on the permittivity.
Fig 4.49: Frequency dependence of the a) real and b) imaginary part of dielectric permittivity ($\varepsilon_\perp'$, $\varepsilon_\perp''$) of FLC-II, at different bias voltages
The variation of dielectric strength and relaxation frequency, at different bias, shows that there is no effect of bias on dielectric strength and relaxation frequency as shown in the Fig 4.51(a) and Fig 4.51 (b) respectively.

The negligible effect of bias on these dielectric parameters can be explained by considering the geometry of the cell. Since the material is in SSFLC geometry, it is well aligned and its helix is unwound due to the effect of surface force. So, its GM is already suppressed and hence there is negligible effect of electric field on the contribution of GM to dielectric permittivity of this FLC material thereby resulting in negligible effect of bias on GM parameters.
Fig 4.51(a):- Bias Dependence of dielectric strength of FLC-II

Fig 4.51(b):- Bias Dependence of relaxation frequency of FLC-II
4.9 Electrical Studies

The current reversal method using capacitor has been used to measure the various electrical parameters of FLC-II. The method has been discussed earlier in detail.

4.9.1 Spontaneous Polarization

4.9.1.1 Temperature Dependence

The temperature dependence of polarization in cell of thickness 6 µm is depicted in Fig. 4.52. It is observed that the temperature dependence of polarization decreases with increasing temperature and is observed to obey the power law as given in eqn.4.6.

![Fig. 4.52: Temperature dependence of polarization in cells of thickness 6 µm](image)

The magnitude of spontaneous polarization corresponds to the one provided in the catalogue by the manufacturer. The critical exponent (β), as obtained from theoretical fit, is found to be 0.49 for FLC-II. The small deviation from the theoretical value of 0.5 is due to the field induced terms, error in measurements and experimental conditions.
4.9.1.2 Bias Dependence

Since the material was in SSFLC mode it did not show any effect of bias on it as shown in Fig 4.53.

![Bias Dependence Graph]

4.9.2 Response Time

**Fig 4.53**: Magnitude of polarization as a function of bias voltage for cell of thicknesses 6 µm

The slope of polarization section gives a measure of rise time.

4.9.2.1 Temperature Dependence

The temperature dependence of τ in cells of thickness 6 µm is depicted in Fig. 4.54

![Temperature Dependence Graph]

**Fig 4.54**: Temperature dependence of response time in cell of thickness 6 µm
It is observed that the temperature dependence of $\tau$ obeys the same trend as given by an Arrhenius law. The response of the material to the applied pulse becomes sharper resulting in a faster response with increase of temperature.

4.9.2.2 Bias dependence
There is no significant effect of bias on response time as shown in Fig 4.55 after threshold value of field.

![Response Time vs Bias Voltage](image)

**Fig 4.55:** Response time as a function of bias voltage for cell of thickness 6 $\mu$m

4.9.3 Rotational Viscosity

4.9.3.1 Temperature Dependence
The rotational viscosity is obtained from the product of spontaneous polarization and response time of the liquid crystals mixture. The temperature dependence of the rotational viscosity is shown in the Fig. 4.56. It also follows the Arrhenius law as predicted by theory. The viscosity of the material decreases with temperature [Fig
4.56] and this decreasing value of viscosity is also a reason for faster response of the material near the transition temperature.

4.9.4 Activation Energy

The activation energy of the material can be obtained by fitting the Arrhenius law to the rotational viscosity vs. temperature curve. Activation energy of the material in the SmC* phase comes out to be 0.47eV. Same value is also obtained by fitting the curve from the variation of relaxation frequency with temperature. However, the temperature dependence of the activation energy can be calculated at a particular frequency by using the equation

\begin{equation}
E_a = RT \left[ 22.92 + \ln \left( \frac{T}{f} \right) \right]
\end{equation}

(4.21)

where R is a gas constant, T is the temperature and f is the relaxation frequency in case of FLCs. The temperature dependence of activation energy can be predicted from this equation.
4.9.5 Azimuthal Angle

The variation of azimuthal angle as a function of temperature for FLC material as calculated with the help of capacitance method is shown in Fig. 4.57. It is found to remain almost constant in the SmC* phase and finally increases sharply after a decrease near the phase transition temperature. Since the azimuthal angle is related to the wave vector by relation $\phi_0 = qz$, it follows the trend similar to wave vector. According to the theoretical predictions the variation of wave vector of pitch with temperature follows the equation (Khoo et. al. 1993, Carlsoon et. al. 1998 & 1988, Levestik et. al 1987, Fillipic et. al 1988)

$$q = \frac{\lambda}{k_3} + \frac{\mu}{k_3} \frac{P_o}{\theta_o} + \frac{d\theta_o^2}{k_3}$$

Where ‘q’ is a wave vector of the pitch, $K_3$ elastic modulus, $\mu, \lambda$ are coefficients of Lifshitz term responsible for flexo-electric bilinear coupling. At low temperature, it slowly decreases with rise in temperature, reaches a minimum value and then finally rises to a finite value at the transition temperature. Our experimental results for temperature dependence of azimuthal angle, as in Fig 4.57, show the same behavior as that of the theoretical curve for q (Carlsoon et. al 1998, 1988, Levestik et. al 1987, Fillipic et. al 1988).
D. Guest-Host Mixture

4.10 Dielectric studies

4.10.1 Frequency Dependence
The guest-host mixture of FLC-II has been prepared with 0.2% wt concentration of MWCNTs. The effect of CNTs on the complex permittivity is reflected in terms of its frequency dependence in SmC* and SmA phases, as shown in Fig. 4.58(a, b) and Fig. 4.59(a, b) respectively. The relaxation of a mode at a particular frequency follow-on to the dispersion of $\varepsilon'$ whereas a peak is observed in the $\varepsilon''$. This frequency corresponds to the relaxation frequency of the mode. Fig. 4.58 and 4.59 shows the presence of some relaxation modes at lower and higher frequencies in both the mixtures. These relaxation modes in SmC* and SmA* phases are reflected in Fig 4.60 in the form of Cole-Cole plots.

In SmC* phase the relaxation at $\sim$1 kHz is observed in both the samples which corresponds to the relaxation of GM. This mode is dominant in the SmC* phase and its contribution vanishes at temperatures well in the SmA* phase due to the complete unwinding of helix in both the samples. In case of pure mixture the GM is observable only up to 1 °C above in SmA* phase with relaxation frequency $\sim$20 kHz. However in case of doped sample it show a comparatively larger contribution and appears up to 6 °C above in SmA* phase with relaxation frequency of $\sim$2 kHz. This is also confirmed by the facts that decrease in $\varepsilon'$ in case doped sample after $T_{C^A}$ is less as compared to pure sample. We are also able to observe a new relaxation mode (NRM) at frequencies ($\sim$50 Hz) lower than the relaxation frequency of GM in case of pure mixture up to a few degree above in SmA* phase. This mode does not appear in CNT doped mixture or is probably masked by the more dominant GM. The overlapping of modes is also observable from the distorted shaped of Cole-Cole plots in Fig 4.60 (b). The presence of various relaxation modes (SM, GM and NRM in pure and SM and GM in Doped FLC) in SmA* is confirmed by the Fig 4.60(b) and inset 4.60(b) showing Cole-Cole plots.

The comparison of pure and doped mixtures shows an increase in real ($\varepsilon'$) and imaginary ($\varepsilon''$) part of permittivity with addition of CNTs in the SmC* phase contrary to the results obtained in case of FLC-I which is a DHFLC material.
increase in permittivity in the SmA* phase on CNT addition is however similar to FLC-I.

**Fig 4.58(a, b):** Frequency dependence of the real and imaginary part of dielectric permittivity ($\varepsilon', \varepsilon''$) of pure FLC-II and its 0.2% CNTs doped mixture at different temperatures in SmC* Phase
Fig 4.59(a, b): Frequency dependence of the real and imaginary part of dielectric permittivity ($\varepsilon'_\perp, \varepsilon''_\perp$) of pure FLC-II and its 0.2% CNTs doped mixture at different temperatures in SmA* Phase.
The temperature dependence of these mixtures shows a dispersion in permittivity to a very small value in SmA phase after exhibiting a hump near the transition temperature, Fig 4.61(a, b). However, far below the transition temperature magnitude of complex permittivity shows a saturated value. We notice an overall increase in permittivity in the SmC* phase with addition of CNTs (Figure 4.61)

Fig. 4.60:- Cole-Cole plots in the SmC* and SmA phase for Pure and 0.2% CNTs doped Sample Inset: the relaxation at frequencies > 5kHz

4.10.2 Temperature Dependence

The temperature dependence of these mixtures shows a dispersion in permittivity to a very small value in SmA phase after exhibiting a hump near the transition temperature, Fig 4.61(a, b). However, far below the transition temperature magnitude of complex permittivity shows a saturated value. We notice an overall increase in permittivity in the SmC* phase with addition of CNTs (Figure 4.61)
which is followed up to the SmA* phase (Figure 4.61). These experimental results led us to believe that in SSFLC structure the permittivity shows an opposite effect in SmC* on CNTs addition than in case of ferroelectric liquid crystal possessing deformed helix ferroelectric structure.

![Graph](image)

**Fig 4.61:** Temperature dependence of dielectric permittivity of Pure and G-H derivatives of FLC-II
4.10.3 Dielectric Strength and Relaxation Frequency

The temperature dependence of the dielectric strength ($\Delta \varepsilon_G$) of the GM, as shown in Figure 4.62, shows an increase in SmC* phase followed up to $T_{C^*}$ on CNTs addition. The dielectric strength ($\Delta \varepsilon_S$) of SM (SmA* phase) was not possible to measure due to incomplete Cole-Cole plots. The dielectric strength of NRM and GM in doped sample also could not be measured due to overlapping [Fig 4.60(b)]. The temperature dependence of the relaxation frequency for GM ($f_G$) is shown in Figure 4.63. The relaxation frequencies of the GM show a slight increase on CNTs addition.

![Figure 4.62: Temperature dependence of dielectric strength of Pure and guest host derivatives of FLC-II](image1)

![Figure 4.63: Temperature dependence of relaxation frequency of Pure and guest host derivatives of FLC-II](image2)
4.11 Electrical Studies

4.11.1 Spontaneous Polarization

The temperature dependence of the polarization for pure mixtures and its G-H derivative is shown in Fig. 4.64. Both the mixtures show an Arrhenius dependence of polarization and fit to the curves gives almost the same value of critical exponent as obtained from the mean field theory. We notice an overall increase in polarization in the SmC* phase with addition of CNTs (Fig. 4.64). This effect of CNTs is continued till the transition to the SmA* phase. It may be due to the presence of already unwound helix in the SmC* phase due to surface forces as addition of CNTs only results in some induction of tilt angle variations and hence results in increase of polarization with CNTs. Also on addition of CNTs, surface anchoring increases and the dipole moment of CNTs also contributes to the polarization. As a result the polarization increases in nanocomposites.

![Variation of spontaneous polarization as a function of reduced temperature for pure and guest host mixtures](image)

Fig 4.64: Variation of spontaneous polarization as a function of reduced temperature for pure and guest host mixtures
4.11.2 Response Time
The variation of response time of pure and doped FLCs as a function of reduced temperature ($\Delta T = T - T_{{C^*}}$, $T_{{C^*}}$ is transition temperature from SmC*-SmA* phase) is presented in Fig. 4.65. It shows that after doping with CNTs, an improvement (decrease) in response time is obtained in the SmC* phase followed up to the SmA* phase. The reduction of response time of LC is highly desirable for large number of applications. This opens a possible application of CNT doped FLC to the LCD industry.

![Image of graph showing response time vs. reduced temperature]

Fig 4.65:- Variation of response time as a function of reduced temperature for pure and guest host mixtures

4.11.3 Rotational Viscosity
The temperature dependence of the rotational viscosity, Fig. 4.66, also shows a decrease in SmC* phase on CNTs addition.
4.12 Theoretical Explanation

The variations in dielectric and electrical parameters are attributed to the increase of surface anchoring energy and effect on SSFLC molecular packing, on CNTs inclusion. The structure of these phases is discussed in equation 4.22 and 4.23 and the relations for $\Delta \varepsilon$, $\varepsilon^*$, $f_G$, $P$, $\tau_S$ and $\gamma_\phi$ are given in equation 4.24-4.31. The equations 4.24 to 4.27 are valid in both SmC* and SmA* phases. In each phase it corresponds to the parameters of modes present in that temperature range. The eqn 4.27-4.31 are valid only in SmC* phase as polarization measurement are not possible in SmA* phase.

First of all we take the effect of doping of CNTs on SSFLC molecular packing. It perturbs the spontaneous polarization (Fig 4.64) and hence response time as well as the rotational viscosity and dielectric parameters. The doping of CNTs affects the packing of DHFLC and reduces its chirality. Theoretically, dilution of the chiral content increases pitch and reduces wave vector (Blinov et al. 1994, Stegemeyer, et al. 1995, Collings, et al. 2003) which according to equation (4.27) reduces the
polarization of DHFLCs (Blinov et. al. 1994, Stegemeyer, et. al. 1995, Collings, et. al. 2003). However, it is well known that SSFLC materials are long pitched and hence their helix is already unwound due to effect of surface forces. The doping of CNTs therefore has little effect on helix and hence on SSFLCs pitch. The dipole moment of CNTs rather add to polarization resulting in its increased value in SmC* phase. Also in SSFLC material the contribution of dipole-dipole interactions between CNTs’ and FLCs’ molecules become significant as compared to dilution of the chiral content resulting in increase of polarization. The increased value of polarization in SmC* phase also decreases response time.

The decrease in rotational viscosity is attributed to the fact that both CNTs and FLC molecules experience a torque due to their nontrivial dielectric anisotropies on the application of electric field. This also reduces the response time of (Equation 4.30) CNT doped SSFLC material.

Next, we take the effect of anchoring energy that reduces response time in CNTs-doped SSFLC material. It has been observed that CNTs increase the surface anchoring by one order of magnitude (Biradar et. al. 1989). The increase in anchoring energy is due to the π-π electron stacking between CNTs, surface alignment layer, and FLC molecules (Lu et. al. 2008, Jeon et. al. 2007, Park et. al. 2007). The relation of response time with the anchoring energy for strong and weak anchoring, respectively, are expressed as follows (Nie et. al. (2007):

$$\tau = \frac{\gamma_\phi}{K_\phi \pi^2} \left( d^2 + \frac{4dK_\phi}{W} \right)$$  \hspace{1cm} (4.32)

$$\tau = \frac{4\gamma_\phi d}{W\pi^2}$$  \hspace{1cm} (4.33)

where $d$ is cell gap, and $W$ is the anchoring energy strength coefficient. Since, cell gap in our case is fixed, so $d$ will not affect much in above equations. In cases, strong anchoring or weak anchoring, the LC response time is inversely proportional to the anchoring energy. The increased anchoring energy lowers the response time in nano-composite. The eqn 4.31 also shows that decrease of rotational viscosity is one of the reasons behind the decrease of response time.
The increased value of polarization can increase response time, as is evident from eqn 4.28, but the combined effect of anchoring energy and rotational viscosity dominate thereby reducing response time.

The change in dielectric parameters can also be explained by the above considerations. As discussed, the addition of CNTs increases polarization. So, the increase in the dielectric constant of Goldstone mode (Figure 4.62) is expected as it depends on the square of polarization which is increasing [Equation (4.24)]. Using Equation (4.25), we can say that, this further increases the permittivity of SmC* as is observed in Figure 4.58. The relaxation frequency of GM that depends on the ratio of polarization and dielectric strength, however, does not show much change in its value (Figure 4.63).

In the SmA* phase also the increase in dielectric parameters is again due to the dipole moment of CNTs and dipole-dipole interactions inducing tilt angle variations which further increases the dielectric strength and dielectric constant. The significant contribution of GM in SmA* phase in case of doped sample also conforms to the presence of tilt angle variation induced by the CNTs. This results in much less changes in permittivity in case of doped mixture after the transition and hence transition temperature appears to be shifted. It is seen from the temperature dependence of permittivity (Figure 4.61) where doped sample shows negligible change in magnitude of permittivity. The transition temperatures are then confirmed by the polarizing microscopy and DSC. The photographs of the pure and doped samples are given in Plate 4.2 and Plate 4.3 respectively representing the disappearance of helical line after the transition in to SmA* phase.
Plate 4.2: The textures of the Pure FLC in (a) SmC* and (b) SmA* Phase
Plate 4.3: The textures of the CNT doped FLC in (a) SmC* and (b) SmA* Phase
Part –3
FLC-III
FLC-827
Geometry
Short Pitch Bisatble Ferroelectric Liquid Crystal mixture

Due to the large sample thickness to helical pitch ratio ($d_S >> p_0$), and small pitch as compared to the wavelength of light used and strong surface treatments, we consider that the cell is in the Short Pitch Bisatble ferroelectric liquid crystal state

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Transitions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure FLC</td>
<td>SmC*- 60°C-SmA*- 73°C –N - 90°C- I</td>
</tr>
<tr>
<td>FLC+0.2% CNT</td>
<td>SmC*- 60°C-SmA*- 73°C –N - 90°C- I</td>
</tr>
<tr>
<td>FLC+0.6% CNT</td>
<td>SmC*- 60°C-SmA*- 73°C –N - 90°C- I</td>
</tr>
<tr>
<td>FLC+0.8% CNT</td>
<td>SmC*- 60°C-SmA*- 73°C –N - 90°C- I</td>
</tr>
</tbody>
</table>
E. Pure Mixture

4.13 Dielectric Studies

4.13.1 Frequency Dependence
Frequency dependence of the real and imaginary part of dielectric permittivity ($\varepsilon'_\perp$, $\varepsilon''_\perp$) of FLC-III, in 6 µm cell, at different temperatures is shown in Fig 4.67(a, b) and Fig 4.68(a, b) respectively for the SmC* and SmA phases. It reflects the dielectric spectrum in the form of absorption ($\varepsilon''$) [Fig 4.67 & 4.68(b)] and dispersion ($\varepsilon'$) [Fig 4.67 & 4.68(a)] curves. It is seen that $\varepsilon'$ shows dispersion at a particular frequency. The saturation in the permittivity is observed after this frequency. On the other hand, $\varepsilon''$ first increases with the increase of frequency to its maxima and then decreases. The position of peak corresponds to the relaxation frequency and occurs at a frequency at which the real part falls to half of its value. This peak in our results corresponds to the relaxation frequency of $GM$ ($f_{GM}$) below transition. The position of peak with respect to the frequency axis shifts to very high value near transition temperature and in the SmA* phase and is the relaxation frequency of $SM$. The $GM$ dielectric spectrum lies in the frequency range up to 10kHz. For FLC-III, the $f_{GM} = 740$ Hz at room temperature as calculated from this peak and that of $SM$ seems to be above 10 MHz, the range of the LCR set up. Fig 4.69 shows relaxation process in the form of Cole-Cole plot at different temperatures.
Fig 4.67: Frequency dependence of a) real and b) imaginary part of permittivity of FLC-III, in 6 µm sample cell, at different values of reduced temperatures (°C) in the SmC* phase
Fig 4.68: Frequency dependence of the a) real and b) imaginary part of dielectric permittivity of FLC-III, in 6µm cell, at different values of reduced temperatures ($\theta$) in the SmA phases.
4.13.2 Temperature Dependence

The temperature dependence of complex permittivity at different frequencies is shown in Fig 4.70(a, b). Fig 4.70(a, b) shows a sharp decrease at the transition...
temperature. However far below the transition temperature the permittivity shows a saturated value. It is due to the decreases in contribution of GM with the increase of temperature and finally at the transition temperature the GM vanishes following very low permittivity. However in Fig 4.70(b) a hump is observed just below the transition temperature due to the significant contribution of two modes i.e. SM and GM. As seen in Fig.4.68–Fig.4.70, there is a pronounced dispersion region below 700 Hz connected with the GM in the SmC* phase. However, near TC*A, a new relaxation region shows up, but its dispersion takes place at much higher frequencies (above 10 MHz) in comparison to GM. This pretransitional relaxation mode is defined as SM, which appears due to the amplitude fluctuations of tilt angle. Fig.4.69 reflects the GM and SM in SmC* and SmA phase in the form of Cole-Cole plot. It is seen from Fig.4.69, that only GM appears at lower temperatures, whereas both GM and SM appears near TC*A and in the SmA phase.
Dielectric strength is the maximum capacity of a capacitor to hold the charge and is related to the dielectric susceptibility as \( \chi = \varepsilon_a \Delta \varepsilon \). The dielectric strength has been calculated using Eq. (2.9). Fig. 4.71 shows the temperature dependence of the dielectric strength (\( \Delta \varepsilon \)) of GM (calculated in case of 6 \( \mu \)m cell) and SM in the absence of an external bias in SmC* and SmA phase of FLC-III. It is observed that the GM dielectric strength (\( \Delta \varepsilon_{GM} \)) in the SmC* phase remains almost constant with temperature and then decreases sharply at the transition after showing a small hump just below the transition temperature.

**Fig 4.70:** Temperature dependence of the real and imaginary part of dielectric permittivity (\( \varepsilon'_\perp, \varepsilon''_\perp \)) of FLC-III, in 6\( \mu \)m cell, at different Frequencies

**4.13.3 Dielectric Strength**

Dielectric strength is the maximum capacity of a capacitor to hold the charge and is related to the dielectric susceptibility as \( \chi = \varepsilon_a \Delta \varepsilon \). The dielectric strength has been calculated using Eq. (2.9). Fig.4.71 shows the temperature dependence of the dielectric strength (\( \Delta \varepsilon \)) of GM (calculated in case of 6 \( \mu \)m cell) and SM in the absence of an external bias in SmC* and SmA phase of FLC-III. It is observed that the GM dielectric strength (\( \Delta \varepsilon_{GM} \)) in the SmC* phase remains almost constant with temperature and then decreases sharply at the transition after showing a small hump just below the transition temperature.
This behaviour of $\Delta \varepsilon_\perp$ can be explained on the basis of the following relation

$$\Delta \varepsilon_\perp = \frac{1}{K} \left( \frac{pP}{\theta} \right)^2$$

where $p$ is pitch, $P$ is the polarization, $K$ is twist elastic constant and $\theta$ is the tilt angle. Below $T_C$ an increase of polarization-tilt ratio and increasing pitch causes the strong increase of dielectric strength. Far from the transition, this ratio is almost constant and the small decrease is due to the decrease of pitch. The twist elastic constant is almost independent of temperature.

Near $T_{C^*A}$, $SM$ starts appearing which shows the characteristic V-shape of dielectric strength in the vicinity of $T_{C^*A}$ as described by mean field model and Curie-Weiss law $f_{SM} = a' + b'(T - T_{C^*A})$, where $a'$ and $b'$ are constants.

**Fig 4.71:** Temperature dependence of Dielectric strength of the GM
4.13.4 Relaxation Frequency

Relaxation frequency has been calculated by fitting the experimental data points plot of \( \log_{10}(V/U) \) versus \( \log_{10}f \), as discussed earlier in the Section 4.3.4 of this chapter. The temperature dependence of relaxation frequency of \( GM (f_{rGM}) \) and \( SM (f_{rSM}) \) in 6\( \mu \)m is shown in Fig. 4.72. These values of \( f_r \) corresponds to the values found from the peak of \( \varepsilon_{\perp}^{\prime\prime} \) [Fig. 4.67 and 4.68(b)]. It is observed that \( f_{rGM} \) in SmC* phase remains almost constant below \( T_{C^*A} \) after which \( SM \) starts appearing. The temperature dependence of relaxation frequencies follows an Arrhenius type of behaviour.

4.13.5 Bias Dependence

The effect of bias on the complex permittivity is shown in Fig. 4.73 for real and imaginary part of permittivity in 6\( \mu \)m cell. The bias dependence in terms of Cole-Cole plots is also represented in the Fig. 4.74.
Fig 4.73: Frequency dependence of the a) real and b) imaginary part of dielectric permittivity ($\varepsilon_\perp'$, $\varepsilon_\perp''$) of FLC-III, at different bias voltages.
It is observed that permittivity decreases on application of bias but the effect is less as compared to FLC-I having DHFLC structure. The variation of dielectric strength and relaxation frequency at different bias is also studied as shown in the Fig 4.75(a) and Fig 4.75 (b). It is observed that there is a decrease in dielectric strength with bias whereas the relaxation frequency increases slightly. These results can be explained by considering the geometry of the cell. Since the material is in SBFLC geometry, its helix is not completely unwound by the effect of surface force. So, its GM is not suppressed and hence there is a decrease in permittivity and dielectric strength on application of bias. However the effect of bias is less as compared to FLC-I having DHFLC structure with completely wound helix.
Fig 4.75(a):- Bias Dependence of dielectric strength of FLC-III

Fig 4.75 (b):- Bias Dependence of relaxation frequency of FLC-III
F. Guest-Host Mixture

4.14 Dielectric studies

4.14.1 Frequency Dependence

The guest-host mixtures of FLC-III have been prepared with 0.2%, 0.6% and 0.8% wt/wt concentration of MWCNT. The effect of CNTs on the complex permittivity is reflected in terms of its frequency dependence in SmC* and SmA phases, as shown in Fig. 4.76(a, b) and Fig. 4.77(a, b) respectively. The relaxation of a mode at a particular frequency follow-on to the dispersion of $\varepsilon'$ whereas a peak is observed in the $\varepsilon''$. This frequency corresponds to the relaxation frequency of the mode.

The comparison of pure and dyed mixtures shows a decrease in real ($\varepsilon'$) and imaginary ($\varepsilon''$) part of permittivity with increase in CNTs concentration in the SmC* phase but an increase in permittivity is observed in the SmA phase. Interestingly, at higher frequencies, the value of $\varepsilon'$ increases even in the SmC* phase with addition of CNTs. The increase of CNT concentration to more than 0.6% also results in the increased magnitude of complex permittivity in SmC* Phase as compared to pure FLC cells.

Fig. 4.78 and 4.79 presents the variation of the real ($\varepsilon'$) and imaginary ($\varepsilon''$) part of the permittivity at different values of reduced temperature ($\Delta T = T-T_{C*A}$, where $T_{C*A}$ is the temperature of the SmC*-SmA phase transition) in the pure and 0.2 % CNTs doped materials. We notice an overall decrease in permittivity in the SmC* phase with addition of CNTs (Figure 4.78), whereas it increases in the SmA* phase (Figure 4.79). A comparison between $\varepsilon'$ values in Figure 4.78(a) and 4.79(a) reveals that $\varepsilon'$ in SmC* phase is about 3 times greater than the $\varepsilon'$ in SmA* phase for pure mixture but this difference narrows down to about 0.25 times for 0.2 wt% CNTs addition. These results are similar to those obtained in case of FLC-I.
Fig 4.76: Frequency dependence of the a) real and b) imaginary part of dielectric permittivity ($\varepsilon_\parallel''$, $\varepsilon_\parallel''$) of pure FLC-III and its guest-host mixtures in SmC* phase
Fig 4.77: Frequency dependence of the (a) real and (b) imaginary part of dielectric permittivity ($\varepsilon_\perp'$, $\varepsilon_\perp''$) of pure FLC-III and its guest-host mixtures in SmA* phase.

250
Fig 4.78(a, b): Frequency dependence of the real and imaginary part of dielectric permittivity ($\varepsilon_\perp', \varepsilon_\perp''$) of pure FLC-III and its 0.2% CNTs doped mixture at different temperatures in SmC* Phase.
**Fig 4.79(a, b)**: Frequency dependence of the real and imaginary part of dielectric permittivity ($\epsilon'_\perp$, $\epsilon''_\perp$) of pure FLC-III and its 0.2% CNTs doped mixture at different temperatures in SmA* phase.
4.14.2 Temperature Dependence

The temperature dependence of all these mixtures shows a dispersion in permittivity to a very small value in SmA phase after giving a hump near the transition temperature, Fig 4.80. However, far below the transition temperature magnitude of complex permittivity shows a saturated value. We notice an overall decrease in permittivity in the SmC* phase with addition of CNTs (Figure 4.80), whereas it increases in the SmA* phase (Figure 4.80). These experimental results indicate that the permittivity shows an opposite effect in SmC* than in SmA phase on CNTs addition in ferroelectric liquid crystal possessing short pitch structure.

4.15 Theoretical Explanation

These variations are attributed to the change of elastic constant and effect on FLC molecular packing, on CNTs inclusion. The detail of these considerations, structure of SmC* and SmA* phases and the equations for dielectric parameters of their relaxation modes (Eqn 4.23-26) have been discussed earlier in this chapter.

First of all we take the effect of elastic energy on dielectric parameters in CNTs-doped DHFLC material. The elastic modulus of CNTs is much larger than that of FLC (Yu et. al. 2000). The strong interaction between CNTs and DHFLC molecules increases the elastic energy of DHFLC molecules and therefore attributed to the increase in elastic constant in the CNT-doped LCs (Jeon et. al. 2007). According to Equation (4.24) and Equation (4.25) it decreases the permittivity in the SmC* phase. Next we consider the change in physical parameters due to the intrinsic properties of FLC material. The doping of CNTs affects the packing of SBFLC and reduces its chiral content. Theoretically dilution of the chiral content increases pitch (Blinov et. al. 1994, Stegemeyer, et. al. 1995, Collings,et. al. 2003) which further reduces the polarization (Blinov et. al. 1994, Stegemeyer, et. al. 1995, Collings,et. al. 2003). The reduction in the dielectric constant of Goldstone mode is expected as it depends on the square of polarization which is decreasing [Equation (4.24)]. Using Equation (4.25), we can say that, this further decreases the permittivity of SmC* as is observed in Figure 4.76. The relaxation frequency of GM that depends on the ratio...
of polarization and dielectric strength, however, does not show much change in its value Figure 4.76-79.
In SmA* phase, only soft mode contribute to the permittivity. The transition from SmC* to the SmA* phase, in CNT-LC mixture (Figure 4.80), seems to be less abrupt increasing the tilt angle variation. The contribution of the soft mode increases simply due to the tilt angle variations. It further increase the complex permittivity of SmA* phase (Figure 4.79) and hence the dielectric strength. Moreover the increased dipole-dipole interaction between CNTs and liquid crystal molecules increases the permittivity. The decrease of permittivity at higher frequencies can also be explained by considering the effect of dipole-dipole interactions. At higher frequencies, the effect