THESIS

On

‘Morphological and Dielectric Behaviour of Dye Dispersed Ferroelectric Liquid Crystal Composite Films’

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Submitted By

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Certificate

This is to certify that the thesis entitled "**Morphological and dielectric behaviour of Dye dispersed Ferroelectric liquid crystal composite films**" submitted by **Preeti Makkar** in the partial fulfilment of the requirement for the award of the degree of **M.Tech.** in **Materials Science and Engineering** from the School of Physics and Materials Sciences, Thapar University, Patiala, is a record of candidate's own work carried out by her under my supervision and guidance. The experimental matter embodied in this report has not been submitted in part or full to any other university or institute for the award of any degree.

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Preeti.

Preeti Makkar

Abstract

The dielectric spectroscopy and electrooptic response of the ferroelectric liquid crystal mixture SCE9 doped with different concentrations of antraquinone dye upto 2.0 wt% has been studied in the frequency range 50Hz-1MHz.Our finding shows that with the dispersion of dye molecules,the SmC*-SmA transition temperature shift to lower side.The permittivity increases up to 1.0wt% concentration of dye and then depleated at higher concentration.The effect of dye addition on different parameters such as Goldstone mode relaxation frequency,spontaneous polarisation and rotational viscosity have also been discussed.

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List of Abbreviations and Symbols

LC	Liquid crystal
NLC	Nematic liquid crystal
FLC	Ferroelectric liquid crystal
DDFLC	Dye dispersed ferroelectric liquid crystal
ITO	Indium tin oxide
I	Isotropic
N	Nematic
N*	Cholesteric
SmA	Smectic A
SmC	Smectic C
SmC*	Smectic C*
ε’	Dielectric permittivity
ε”	Dielectric losses
P_s	Spontaneous polarization

CHAPTER-1

INTRODUCTION

This chapter gives us an introduction to the liquid crystals and explains all the various classifications of liquid crystals on the basis of shape, molecular arrangement or structural behaviour. Their physical properties and effect of electric field in LCs is briefly discussed. A comparison between crystalline and LC ferroelectrics is given and the theories involved in present work has been discussed. The scope of the thesis is briefly given at the end of the chapter. The section also the reviews the research work already carried out in dye dispersed FLCs and discuss their dielectric behaviour in particular.

1.1 Overview

Ferroelectricity in liquid crystals is a specific property of some chiral smectic phases. It was first discovered by Meyer et al. in 1975, in a classic liquid crystalline material, p-decyloxy bezylidine p-amino-2-methylbutyl cinnamate (DOBAMBC) exhibiting chiral smectic C (SmC*) phase [7]. Since then considerable experimental and theoretical studies have been carried out to understand the various physical properties of this phase [15]. Ferroelectricity in liquid crystals is the combined property of chirality in the molecule, the tilt angle of the director and smectic-layered structure of the material. The ferroelectric liquid crystals have been explored by a large number of researchers for their use in electro-optical devices [39–40]. Most of the studies on ferroelectric liquid crystals are concentrated around dielectric and optical properties of liquid crystals as these properties are critical for their application in different devices [12]. Till date, a large number of papers dealing with the experimental and theoretical aspects of the dielectric properties of chiral phase of ferroelectric liquid crystal (FLC) molecules have been published [22-26]. FLCs have been receiving the high attention of many researchers because of their fast response time and memory effect. FLCs have been widely used in electro-optical devices, particularly in displays due to their peculiar properties [27–31].Most of the FLC displays are black and white and less durable, because of various components used in displays like polarizer, etc. [32] and suffers from low contrast ratio and small viewing angle. To create an optical contrast in FLC displays, primarily two

modes have been used, the birefringence mode,[33] and the guest host mode.[34] The guest host mode has been investigated in the present study because this mode provides a high quality display with wide viewing angle ,uniform color, high contrast ratio, high brightness and definitely the fast response time.. Also the use of Guest host mode avoids the use of polarizers, partially or fully. Hence, Guest host mode is widely used in the colour displays. [35] The dichroic dye as Guest in liquid crystal matrix in not only applicable in colour displays but they are also very much useful for other applications such as photo voltaic effect and bleaching effect. Many researchers have used various kinds of dyes in order to improve dichroic ratio, particularly Azo and Anthraquinone dyes [36, 37]. In the present work Anthraquinone dye has been used for mixing in FLCs because it posses higher photochemical stability [37, 38].

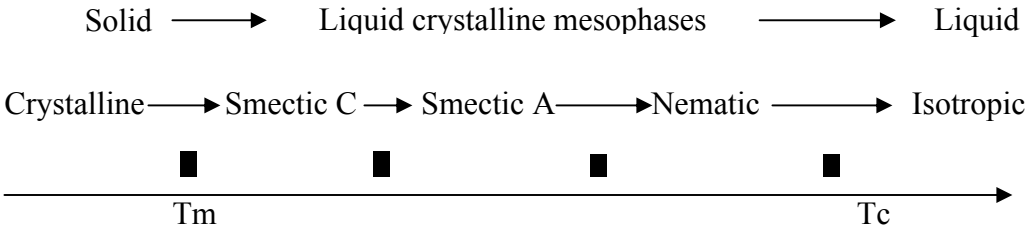
Dielectric spectroscopy of FLC materials has been of increasing interest in the past few years, and studied extensively both theoretically as well as experimentally [13]. The dielectric response below 1MHz mainly consists of two modes in FLCs .These are mainly related with director fluctuations in the form of azimuthal angle fluctuation, i.e., Goldstone mode and tilt angle fluctuation, i.e., soft mode. In SmC* phase Goldstone mode predominates over the soft mode and soft mode comes into existence near the SmC*– SmA phase transition temperature [14]. Addition of dye molecule into the pure FLC mixture results in redistribution of intermolecular energies, hence dielectric relaxation study is of great help to understand the various molecular properties of dye mixed FLC mixture [13].

1.2 Liquid Crystal

Delicate, beautiful, mysterious, dynamic are words, which describe the rich class of liquid crystals. The remarkable work by German physicist Otto Lehman and Austrian botanist Friedrich Reinitzer around 1888 when he prepared cholesteryl benzoate (the first liquid crystal) justified them to be called the grandfather of liquid crystal science. [1-5].

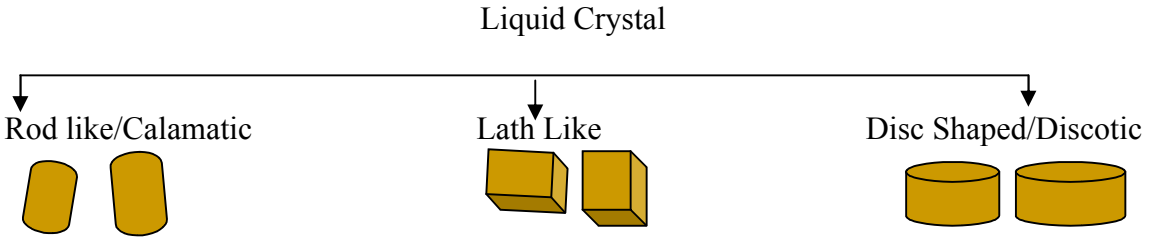
Liquid Crystal signifies a state of aggregation that is intermediate between the crystalline solid and the amorphous liquid. A substance in this state is strongly anisotropic in some of its properties and yet exhibits a certain degree of fluidity. These mesophases are organic compounds with oriented aromatic and aliphatic groups. In the

solid phase, the molecules have a large amount of both positional and orientational order, in that the molecules maintain specific positions and orientations. In the liquid phase, there is no positional and orientational order, since the molecules diffuse about quite randomly, constantly changing both their positions and orientations. In the liquid crystal phase, the molecules can diffuse about, much as they do in liquids, but as they diffuse they are orientationally ordered but positionally disordered [1].



1.3 Classification of Liquid Crystals

On the basis of geometrical structure of the molecule, liquid crystals can be divided into--

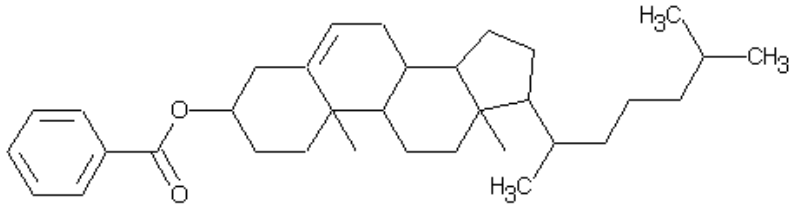


Liquid crystals can be divided from the molecular order standpoint into:

1. Thermotropic
2. Lyotropic

Thermotropic liquid crystals are those, which show mesomorphic behaviour in a definite temperature range. Thermotropic liquid crystals exist in both rod and disc shaped molecules. However, a vast majority of them are composed of rod-like molecules. On the other hand, lyotropic liquid crystalline phases show mesomorphic behaviour by the change in the concentration of the solute in a solution. Calamatic and discotic molecules are the most common forms in which both thermotropic as well as lyotropic liquid crystals exist [5]. Given below some of the earliest important liquid crystals-----

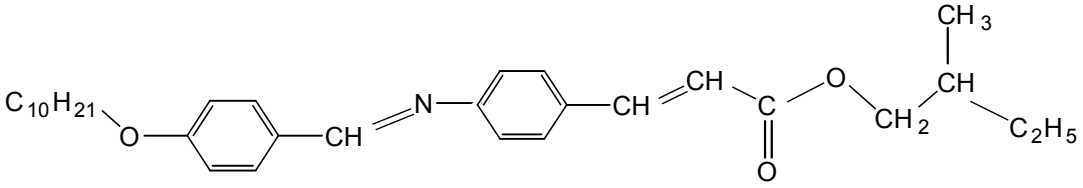
1. First Thermotropic Liquid Crystal



Line notation: **Ph-COO-Cholest-5-ene**

Common abbreviation: **Cholesterol Benzoate(CB)**

2. First Ferroelectric Liquid Crystal



Line notation: **$C_{10}H_{21}$- O-Ph-CH=N-Ph-CH=CH-COO-CH_2-CH-CH_3-C_2H_5**

Common abbreviation: **DOBAMBC**

1.3.1: Liquid Crystal Phases

It was in 1922 that a French scientist named George Friedel [7-8] proposed a classification scheme based on the molecular arrangement where he named different liquid crystal systems: nematic, smectic and cholesterols.

1.3.1a: Nematics (N) Phases

Nematic (N) is the most common and simplest liquid crystal phase. The word "nematic" is derived from the Greek word for "Thread" as thread like textures were observed under the polarizing microscope [1]. In this phase, the molecules possess long range orientational order but no positional order in this phase as shown in fig. 1.2(a).

The orientational order is defined by an average direction of molecules called the DIRECTOR and is denoted by the vector n. In practice, the orientation of individual molecules differs significantly from that direction, thus the nematic phase can be

characterized by an order parameter S. The orientational order parameter S is based on the average of the second order Legendre polynomial and is defined as:

$$S = \langle P_2(\cos\theta)\rangle = \frac{1}{2}\langle 3\cos^2\theta - 1\rangle$$

where < > denotes a thermal averaging, θ is the angle between each molecule and the director and S is the amount of order present in the liquid crystal.

If the molecules are well aligned with the director, then it takes the value 1 and if the molecules are randomly oriented about n, i.e., isotropic, then S=0. So, the higher the order parameter the more ordered the nematic liquid crystal. Typical value for the order parameter is in between 0.3 and 0.9 [1-3].

1.3.1b: Cholesteric Phase

When a nematic phase is incorporated with a chiral molecule, it leads to the formation of a structure as a stack of very thin 2-D nematic like layers with the director in each layer twisted with those above and below (as shown in fig1.1). In this structure, the directors actually form in a continuous helical pattern about the layer normal. An important characteristic of the cholesteric mesophase is the pitch, defined as the distance it takes for the director to rotate one full turn in the helix. The necessary condition for the formation of the cholesteric mesophase is that the molecules are chiral (optically active) that is why cholesteric phase is also defined as the chiral nematic phase, represented by N*[1-2].

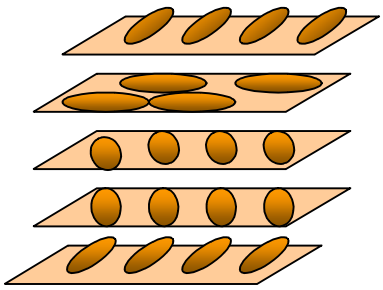


Fig1.1: An arrangement of molecules in cholestric phase.

1.3.1c: Smectic phases

The word "smectic" is derived from the Greek word for soap [1]. The smectic state is another distinct mesophase of liquid crystal substances. They are more ordered as compared to nematic and cholestric liquid crystals. In the smectic state, the molecules

maintain the general orientational order of nematics, but also tend to align themselves in layers or planes [16].

I. **Smectic A phase**

In the smectic-A mesophase, the director is perpendicular to the smectic plane. This phase can be classified as an orientationally ordered liquid on which a 1-D density wave is superimposed as shown in fig1.2 (b).

II. **Smectic C phase**

In the SmC mesophase, molecules are arranged as in the SmA mesophase, but the director is at constant tilt angle measured normally to smectic plane as shown in fig1.2(c)

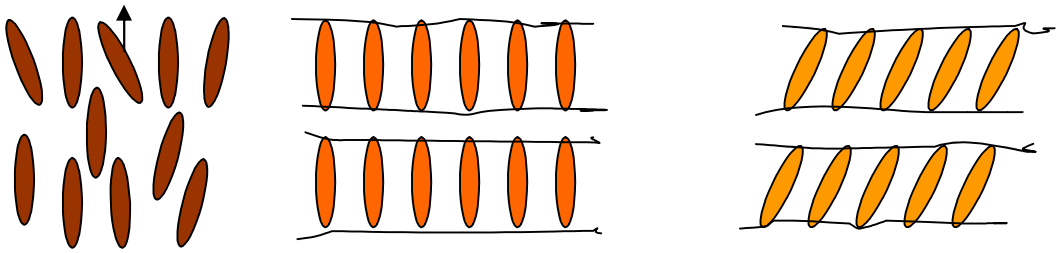


Fig 1.2: Arrangement of molecules in (a) nematic phase (b) smectic A phase (c) smectic C phase.

III. **Chiral smectic C phase**

A chiral molecule (from the Greek word for *'hand'*) is a molecule that cannot be superimposed on its mirror image. Chiral molecules are optically active in the sense that they rotate the plane of polarized light [2,3]. Chiral compounds are able to form mesophases with structures related to those of non-chiral substances, however, with different properties. As in the nematic, the smectic-C mesophase has a chiral state designated C*.

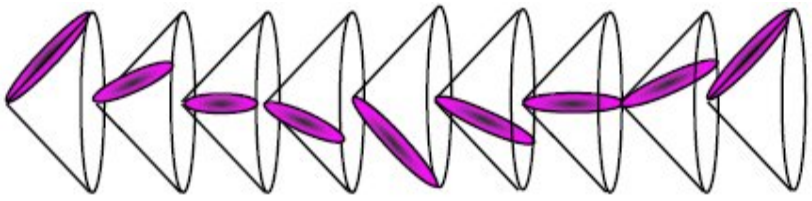


Fig1.3: Arrangement of molecules in SmC*phase (helical)

Consistent with the smectic-C, the director makes a tilt angle with respect to the smectic layer. The difference is that this angle rotates from layer to layer forming a helix (as seen

in fig1.3). In other words, the director of the smectic-C* mesophase is not parallel or perpendicular to the layers, and it rotates from one layer to the next [1].

1.4 Physical properties of Liquid crystals

1.4.1 Anisotrophy in Liquid Crystals

The property of LCs that distinguishes them from liquids is the small degree of order among the molecules. This order destroys the isotropy of liquids and produces anisotropy. The combination of molecular order and fluidity in a single phase results in remarkable properties unique to LCs. Due to the fluidity property, LCs show anisotropy in their behaviour and it is very much evident that they are structurally very anisotropic[1,6].Because of their shape anisotropy, all the molecular response functions, such as the electronic polarizability, are anisotropic. The long range order in the LC phases prevents this molecular anisotropy from averaged to zero, so that all the macroscopic response functions of the bulk material, such as the dielectric constant are anisotropic as well [1,6].

1.4.2 Birefringence in Liquid Crystals

The phenomenon in which the two polarizations have different indices of refraction (ordinary and extraordinary) and therefore travel along two different directions inside the material is called birefringence or double refraction. The anisotropy of NLC causes light polarized along the director to propagate at a different velocity than light polarized perpendicular to the director. NLC are therefore birefringent. However the structure of cholestric LC which has a helical structure and the layered structure of smectic LCs affect the propagation of light differently. In this case circular birefringence takes place [1].

1.5 Electric and Magnetic Field Effects

The response of liquid crystal molecules to an electric field is the major characteristic utilized in industrial applications. The ability of the director to align along an external field is caused by the electric nature of the molecules. Permanent electric dipoles result when one end of a molecule has a net positive charge while the other end has a net negative charge. When an external electric field is applied to the liquid crystal, the dipole molecules tend to orient themselves along the direction of the field. In the following

figure 1.4, the black arrows represent the electric field vector and the red arrows show the electric force on the molecule.

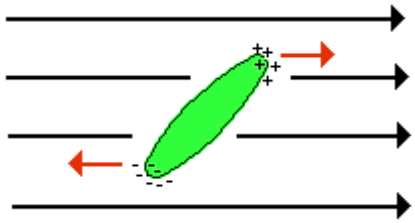


Fig1.4: Influence of electric field on LC molecule

Even if a molecule does not form a permanent dipole, it can still be influenced by an electric field. In some cases, the field produces slight re-arrangement of electrons and protons in molecules such that an induced electric dipole results. While not as strong as permanent dipoles, orientation with the external field still occurs. The effects of magnetic fields on liquid crystal molecules are analogous to electric fields. Because magnetic fields are generated by moving electric charges, permanent magnetic dipoles are produced by electrons moving about atoms. When a magnetic field is applied, the molecules will tend to align with or against the field [3].

1.6 Ferroelectric liquid Crystals

Robert B. Meyer in 1975 creatively utilized symmetry arguments to predict that all chiral smectic phases with tilted structure exhibit ferroelectric properties. This discovery of ferroelectricity in a fluid system with the possibility for unique applications surprised the entire condensed matter research community and quickly paved the way for both increased scientific understanding and significant technological advancement. This leads to further study of ferroelectric liquid crystals (FLC). Due to their low symmetry they are able to exhibit spontaneous polarization and are known as ferroelectric liquid crystals [7]. Spontaneous polarization is the signature and defining characteristic of these ferroelectric liquid crystals. The permanent electric polarization **P** is perpendicular to the director **n** and parallel to the smectic layers. The magnitude of the polarization depends on temperature, generally decreasing as the tilt angle goes to zero at the SmC-SmA phase transition. When the molecule is chiral, successive tilted smectic layers show a gradual change in the direction of tilt, such that the director precesses about the layer normal from layer to layer, always lying on the surface of a hypothetical cone of angle 2θ.

The angle around the circle of precession is known as the azimuthal angle Φ. This creates a helical structure in the tilted chiral smectic mesophases with the pitch being the distance along the layer normal needed to reach the same molecular orientation. In addition to producing this helical structure, chirality results in a spontaneous molecular polarization. Figure 1.5(a) shows the spiral polarization direction in Sm C* phase [11]. Figure 1.5(b) shows the basic geometry of the Sm C* phase. Since the coupling of the polarization to applied fields is linear in the field, this means that FLCs can be made to switch quickly (typically within a few microseconds). This makes FLCs ideally suited to electro-optic applications. Small ferroelectric LCDs have found their way into the viewfinders of digital cameras, cell phones, and pocket computers, while larger displays are used for computer monitors and televisions [16].

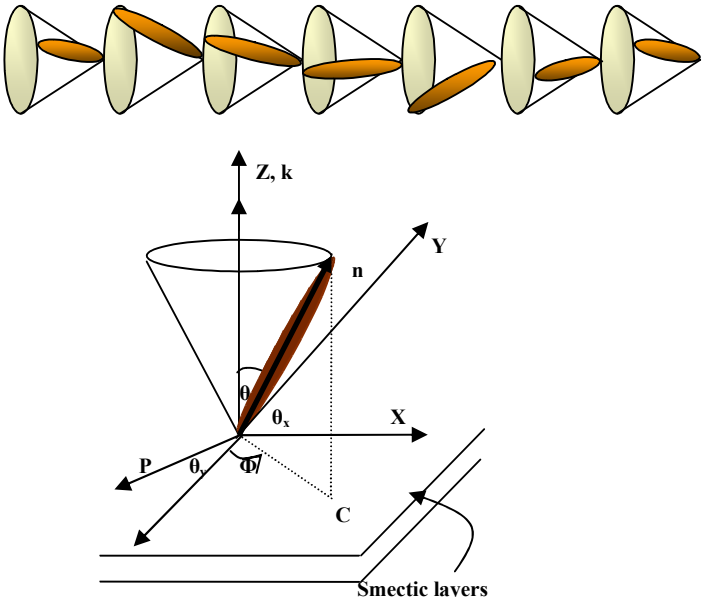


Fig1.5: (a) Spiralling of the director in Sm C* phase. (b) Basic geometry of the Sm C* phase showing layer normal Z, tilt angle□, molecular director n, polarization P along (z x n) and azimuthal angle Φ of P about z. Directions of both n and P vary spatially in a helical manner.

1.7 Comparison with Solid Ferroelectrics

Rochelle salt was the first ferroelectric material to be discovered in 1921. There are interesting similarities and dissimilarities between FLCs and much more studied ferroelectric solid crystals [10, 11]. Making a comparative study, solids ferroelectrics are

inorganic compounds, whereas ferroelectric liquid crystals are organic compounds. Molecules in solids ferroelectrics are arranged in domains and randomly oriented domains lead to zero net dipole moment. In FLCs molecules are arranged in a helicoidal manner due to which the net dipole moment is zero. Typical polarization values for solid ferroelectrics lie around 10^{-7}-10^{-5} C/cm^2. The corresponding values for FLCs are 10^{-9}-10^{-7} C/cm^2. Coercive field is of the order of kV/cm in case of solids ferroelectrics, but is comparatively less in case of FLCs. The Curie Weiss law is obeyed over a wide range of temperature in solids and in a narrow range of temperature in FLCs. In ferroelectric crystals, the polarization is most often the primary order parameter of the ferroelectric phase. On the other hand, in ferroelectric liquid crystals, polarization is the secondary order parameter and it is a structural by product of the symmetry of the tilted chiral smectics. Solid ferroelectrics generally exhibit fast (~10ns) switching with low refractive index changes ($\Delta n \sim 10^{-3}$). Ferroelectric liquid crystal switching is slower (~1μs) but with a much larger change ($\Delta n \sim 0.1$). In $BaTiO_3$ and related materials, the birefringence Δn is zero in the cubic paraelectric phase and $\Delta n \neq 0$ in the ferroelectric phase is directly related to the lattice distortion introduced at the transition. In ferroelectric liquid crystals there is hardly any practical difference between the birefringence values of A* and C* phases. The difference is that in the C* phase this anisotropic axis **n** can be switched around to new directions in space because of its rigid steric relation with the local polarization **P**.

The molecules of SmC form a layered structure and tilt away from the layer normal by an angle □. In the chiral Sm C* phase the constituent molecules are arranged in diffuse layers where the molecules are tilted at a temp dependent angle with respect to the layer planes. The molecules within the layers are locally hexagonally close packed with respect to the director of the phase, however, this ordering is only very short range, extending over distances1.5-2.5nm.Over large distances, therefore the molecules are randomly packed, and in any one domain the molecules are tilted roughly in the same direction[40]

1.8 Antiferroelectric and Ferrielectric Phases

MHPOBC was the first antiferroelectric liquid crystal found by a Japanese group in 1986 [19-20]. Here, the director always lies in the layer plane and the polarization vector perpendicular to it. In subsequent layers the director is pointed in opposite directions and

so is the polarization vector. Thus because of an equal number of polarization vectors pointing up and down, the spontaneous polarization averages out to zero even for the unwound (non helical) state. This structure is evidenced by the fact that when a strong electric field is applied to this phase, the layer ordering is perturbed and the phase returns to a normal ferroelectric phase. In the switching of antiferroelectric phases three states are produced: one antiferroelectric and two ferroelectric [26]. This tristable switching occurs at a defined electric field and thus the presence of a sharp switching threshold may be useful in display applications, which require multiplexing with grey scales. The structure of ferroelectric Sm C* phase is repeated every 360° rotation of the helix, whereas the helical structure of the antiferroelectric phase repeats every 180° rotation. Therefore, the phase appears to have a relatively short pitch and the pitch appears to change quite significantly as the temperature is changed. In the ferrielectric smectic phase, the layers are stacked in such a way that there is a net overall spontaneous polarization. The number of layers of opposite polarization is not equal. It has also been suggested that the stacking of the layers has two interpenetrating sublattices. There are alternating layer structures, i.e., two layers tilted to the right and one to the left, with this arrangement repeating itself throughout the bulk of the phase. Thus, the ferrielectric phase has a measurable polarization. Figure 1.6 shows the difference between ferro, antiferro, and ferrielectric chiral Sm C phases.

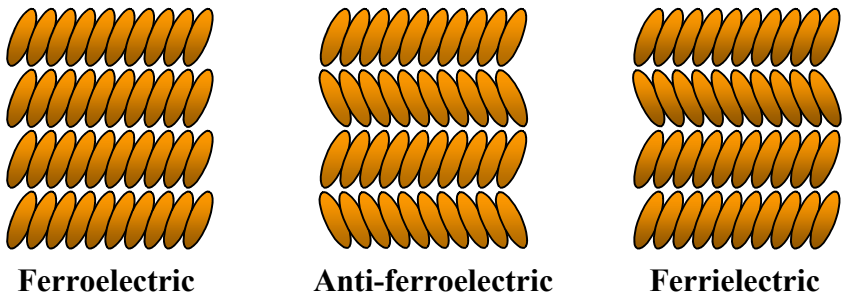


Fig 1.6: The arrangement of molecules in ferro, antiferro and ferroelectric chiral Sm C phases

1.9 Dyes

Dyes can be said to be coloured, ionising and aromatic organic compounds which shows an affinity towards the substrate to which it is being applied. It is generally applied in a solution that is aqueous. Dyes are the largest group that can easily be manipulate to our

liking. Dyes are applied to numerous substrates for example to textiles, leather, plastic, paper etc. in liquid form. One characteristic of dye is that the dyes must get completely or atleast partially soluble in which it is being put to.

1.9.1 Antraquinone Dye

Anthraquinone dyes are the organic dyes having molecular structures based upon that of anthraquinone. The group is subdivided according to the methods best suited to their application. Basically two types of dyes anthraquinone and azo dyes are used as Guest in liquid crystal matrixes. The use of any dichroic dye in liquid crystal matrix depends upon its solubility, order parameter and ionic stability, etc. Therefore the suitable dye for Guest host application must have high order parameter and also the high resistance against the chemical and photolytic degradation, i.e. must not contain any ionic or ionizeable group. The azo dyes normally have high order parameter, which clearly means that they will result in the high contrast ratio. But these dyes are highly photodegradable, where as the anthraquinone dyes show high resistance against chemical and photo degradation [17].
Therefore anthraquinone dye of high order parameter (S = 0.71-0.82) will be more suitable for Guest host mode application. Figure 1.7 shows the molecular formula of antraquinone dye used in the experiment [18]. The following table (table1.1) shows the physical properties of antraquinone dichroic dye used in the experiment. Figure 1.8 shows that how the dye molecule fit in the molecular geometry of pure FLC.

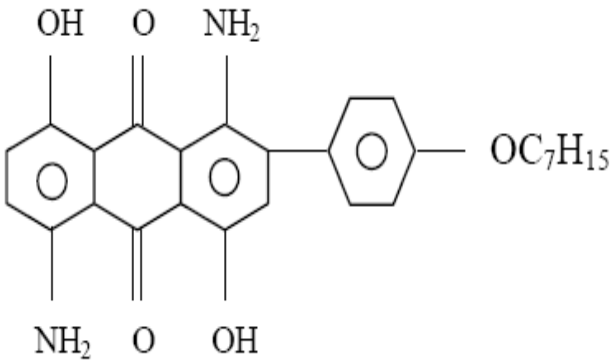


Fig.1.7: Molecular Structure of anthraquinone dye molecule

Table1.1: Physical properties of antraquinone dye

Properties	***Value***
Solubility	100%
Colour	Blue
λ_{max}	630 nm

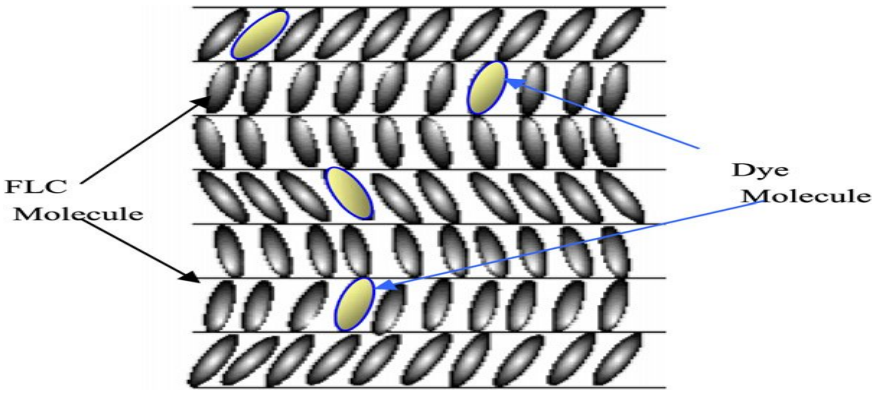


Fig1.8: Schematic diagram showing that how the dye molecule fit in the molecular geometry of pure FLC.

1.10 Theoretical background

Given below the silent features of the theories related to work……..

1.10.1 Dielectric Behaviour in Chiral Smectics

Chiral smectics are complex systems, and certain features of this also appear in their dielectric behaviour. In order to illustrate physical meaning of the dielectric permittivity ε in smectics, time-dependent electric field has been applied in direction parallel or perpendicular to smectic layers and its affect on the dielectric medium is observed, as shown in fig1.9. Let us consider the molecular motions in SmC^* phases. We may categorize them in following types:

Non- collective excitation:

- Molecular rotation around short axis
- Molecular rotation around long axis
- Intramolecular rotation around single bond
- Motions of electrons relative to their nuclei

Collective excitation:

- Soft mode
- Goldstone mode

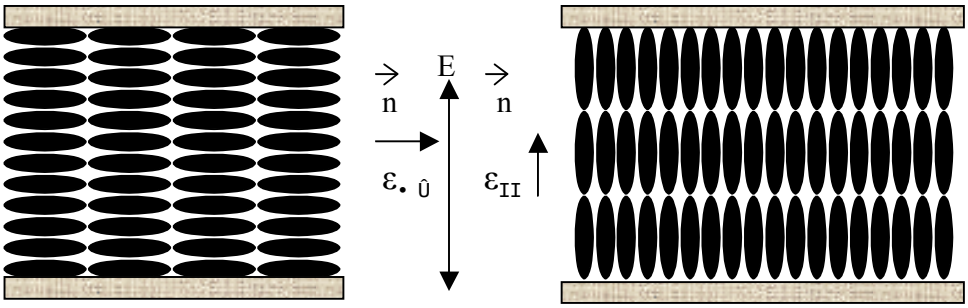


Fig1.9: Two different measuring geometries; electric field E is applied in direction perpendicular, and parallel to direction n, respectively, thus permitting measurement of the two components of the dielectric permittivity

The electric field E when applied to SmC* phases will induce a polarization from each process mentioned above, due to distortion of the symmetric distribution of dipoles. The induced polarization results in an increase in the value of capacitance. Dielectric constant ε is related to average induced polarization $\langle P_{ind} \rangle$ via the relation

$$\varepsilon = \lim_{E \to 0} \frac{\langle P_{ind} \rangle}{E} + 1 \qquad (1)$$

The condition E→0 is to ensure a linear dielectric response [41]. The magnitude of the induced polarization varies when smectic is subjected to a time-dependent electric field. As long as molecular reorientation follows the instantaneous field, induced polarization (or dielectric permittivity) is constant. It is within this frequency range the dielectric permittivity can be denoted by dielectric constant ε_0, and the mode is fully contributing to dielectric permittivity. At higher frequencies where the dipolar reorientation is no longer in phase with the field, the contribution of the mode decreases more and more until it is completely absent. The corresponding value of ε is denoted as ε_∞. This region of the dielectric spectrum is called the relaxation region. At higher frequencies other modes may still be active and contribute toε. Let us denote the contribution of each mode to ε as $\Delta\varepsilon = \varepsilon_0 - \varepsilon_\infty$. Δε is also called dispersion magnitude. Within the relaxation regime there is a phase difference between field (stimulus) and induced polarization (response). Due to this phase difference, a part of electric energy is dissipated in the form of heat. Thus, there is

an energy loss that is absorbed by the dielectric material. Mathematically, this dielectric absorption is accounted for by introducing complex dielectric constant ε*, conveniently written as **ε* = ε′ – iε"**

The imaginary part due to each molecular process goes through a maximum when changing the frequency. For non-collective types of molecular motions, it is the collisions between molecules, which inhibit reorientation. For the collective type of processes, the relaxation times are, generally, governed by viscoelastic properties and may also depend on surface forces.

Debye and Cole-Cole model

A simple model allowing todescribe the relaxation of the dielectric permittivity in terms of a single time constant is due to Debye. The real ε′ and imaginary ε″ parts of the complex dielectric permittivity ε* are written as

$$\varepsilon^* = \varepsilon_\infty + (\varepsilon_o - \varepsilon_\infty)/ (1 + i\omega\tau), \quad (1)$$

$$\varepsilon' (\omega) = \varepsilon_\infty + (\varepsilon_o - \varepsilon_\infty)/ (1 + \omega^2 \tau^2), \quad (2)$$

$$\varepsilon''(\omega) = (\varepsilon_o - \varepsilon_\infty)\, \omega\tau / (1 + \omega^2 \tau^2) \quad (3)$$

where ε_o and ε_∞ are low and high frequency permittivity ,the dielectric increment $\Delta\varepsilon = \varepsilon_o - \varepsilon_\infty$, ω is the angular frequency of the applied field and τ is relaxation time which is related to the relaxation frequency f_R as $\tau = \frac{1}{2}\pi f_R$. Eliminating frequency from equations (2) and (3), equation of a circle is obtained with centre on the ε′ axis, as shown in fig1.10. This graphical representation of equation is called the Cole-Cole plot. The plot is very useful to check if the experimental values of ε′ and ε″ can be described by a single relaxation time, which it often cannot. Many systems show a deviation in this sense from Debye dispersion. In order to describe systems, which do not relax with a single relaxation time, Cole has extended the Debye equation by introducing the distribution parameter α.

$$\varepsilon^*(\omega) = \varepsilon_\infty + (\varepsilon_o - \varepsilon_\infty)/ [1 + (i\omega\tau)^{1-\alpha}]. \quad (4)$$

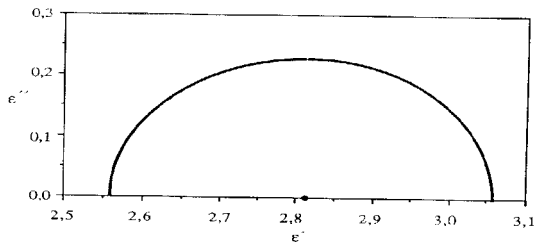


Fig 1.10: Cole-Cole plot showing relation between ε′ and ε′′ for a mechanism with a single relaxation time

1.10.2 Theoretical approach of shifting of phase transition temperature due to dye addition

In the lowest order the mean field expression for the non chiral smectic phase at temperature T can be written as [15]

$$F = F_0 + \frac{1}{2}A(T)\theta^2 \quad (1)$$

where F_0 is the free energy of ground state in smectic Aphase, A(T) the temperature dependent Landau coefficient and may be expressed as A(T) = a(T-Tc), θ is the tilt angle, Tc is the SmC*–SmA phase transition temperature. To extend this expression for chiral SmC* phase, we have to consider the effect of spontaneous polarization. Therefore the mean field expression for the free energy density of chiral molecule may be written as [21]

$$F = F_0 + \frac{1}{2}A(T)\theta^2 + \frac{1}{2}(\chi_P)^{-1}P^2 - CP\theta \quad (2)$$

Here P is the induced polarization, χ_P the high frequency dielectric susceptibility and C the electroclinic coupling constant. Whenever dye is mixed into a pure ferroelectric liquid
crystal the Landau coefficient must be a function of concentration of dye, so A(T) should be replaced by A(T, x). Here x is the concentration of dye in pure ferroelectric liquid crystal mixture. For low orders of T and x, A (T, x) may be expanded as follows:

$$A(T,x) = a(T - T_c) + \lambda x \quad (3)$$

Here l is the coefficient of dye concentration. Hence the modified Landau free energy expression for dye doped ferroelectric liquid crystal system may be expressed as

$$F = F_0 + \frac{1}{2}A(T,x)\theta^2 + \frac{1}{2}(\chi_P)^{-1}P^2 - CP\theta \quad (4)$$

In the equilibrium condition the free energy will be minimum. Therefore,

$$\frac{\partial F}{\partial P} = 0 \quad \text{or} \quad P = C\chi_P\theta$$

Hence Eq. (4) becomes

$$F = F_0 + \frac{1}{2}(A(T,x) - C^2\chi_P)\theta^2 \tag{5}$$

Let

$$A^*(T,x) = (A(T,x) - C^2\chi_P) \tag{6}$$

$$S_0F = F_0 + \frac{1}{2}A^*(T,x)\theta^2 \tag{7}$$

This equation is similar to Eq. (1), so using these equations we can write A*(T, x) as

$$a(T - T^*_{cd}) = a(T - T_c) + \lambda x - C^2\chi_P$$

Hence the transition point of dye-doped system may be written as

$$T^*_{cd} = T_C + C^2\frac{\chi_P}{a} - \frac{\lambda x}{a} \tag{8}$$

Here T^*_{cd} is SmC* to SmA phase transition temperature of dye-doped system. According to Eq. (3) A (T, x) will be zero at transition temperature, i.e., whenever x0, $T^*_{cd} \longrightarrow T_C$, Also T^*_C may be written as

$$T^*_c = T_C + C^2\frac{\chi_P}{a} \tag{9}$$

Using Eq. (8) and (9) we may develop the relation for SmC* to SmA phase transition temperatures of pure ferroelectric liquid crystal and their dye-doped mixture as follows:

$$T^*_{cd} = T^*_C - \frac{\lambda x}{a} \tag{10}$$

Using the same logic we may develop similar type of equation for other phase transition temperatures of pure and dye doped ferroelectric liquid crystals. Thus, the transition temperature is predicted to decrease linearly with increasing dye concentration [16].

1.11 Literature Review

The ferroelectric properties in chiral smectic (SmC*) liquid crystalline phase were first demonstrated by Meyer.et al. in 1975 [7]. Till date, a large number of papers dealing with the experimental and theoretical aspects of the dielectric properties of chiral phase of ferroelectric liquid crystal (FLC) molecules have been published [22–25]. Addition of

dye in ferroelectric liquid crystal (FLC) results in change in many properties of FLCs which depend upon some basic properties of pure FLCs, dye molecular structure and its concentration in pure FLC. Srivastava et al. [17] reported the dielectric and electro-optical studies of pure and dyed FLCs for this aspect. The FLC material used in their work is Felix 17/000 and the antraquinone dye dispersed sample were prepared in the concentrations of about 1%, 2%, 3%, 4% and 5% wt/wt ratio .It was observed by them that after dye dispersion, the SmC*–SmA phase transition temperature shifts towards lower temperature side and this shifting to SmC*-SmA phase transition temperature just follows a straight line with dye concentration. Also, they found the deviation in the values of dielectric permittivity and dielectric loss and predict that the strength of Goldstone mode may increase or decrease. They also observed that the relaxation frequency of Goldstone mode shifts toward higher frequency side for low concentration while for high concentration it shifts towards lower frequency side.

The dielectric spectroscopy of the ferroelectric liquid crystal mixture FLC-6980 doped with a low concentration (2% wt/wt) of anthraquinone dye were reported by Raina.et al. [18]. In their work, the complex permittivity measured in the frequency range 100 Hz to 1 MHz in SmC* and SmA phases. They observed that the relaxation frequency and the SmC*–SmA transition temperature decreases whereas the dielectric increment increases about 2.5-fold on dye addition.

Shukla.et al. [14] used the two ferroelectric liquid crystal samples CS1016 and Felix 17/000 dispersed with anthraquinone dye. They observed that the dielectric behaviour of dye mixed CS1016 is quite different from that of Felix 17/000. The dielectric permittivity of dye dispersed CS1016 is high as compared to pure CS1016 and opposite in case of felix17/000.This different behaviour has been explained by them by determining other parameters like distribution parameter, dielectric strength and relaxation frequency, etc. They observed that SmC*–SmA phase transition temperature decreases for the both mixtures than pure FLCs and the relaxation frequency also followed the opposite change (i.e. it shifts to the higher side for CS1016 and lower side for felix 17/000 with respect to the relaxation frequency of their respective pure FLCs).

Raina.et al. [15] were reported the dielectric spectroscopy of a short pitch and high spontaneous polarization ferroelectric liquid crystal mixture FLC-6304 pure and

dispersed with different wt/wt ratio (1,2,4%) of anthraquinone blue dichroic dye over a wide frequency range of 50 Hz–1MHz. They observed that the increase in dye concentration results in the decrease of the permittivity of the material in the SmC* phase, however, an opposite effect is observed in the SmA phase. The influence of bias voltage on the dielectric parameters was also reported. A new relaxation mode was observed with a relaxation frequency of 300 kHz and dielectric strength ~ 5 was observed at room temperature.

To study the effect of mixing dye in FLC materials, the dielectric and electro-optical properties of FLC material Felix 16/030 pure and dispersed with anthraquinone dye at concentrations of about 1,2and3% wt/wt ratio were reported by Manohar.et al. [13]. They observed that all the properties are strongly dependent on dye concentration in pure FLC. The pre-transition phenomenon reduces by the addition of dye molecule into pure FLC mixture and the values of dielectric permittivity changes which depend upon the concentration of dye in pure FLC. It was observed that the relaxation frequency of Goldstone mode shifts toward high or low frequency side suggested that Goldstone mode for high concentration became slower than the lower concentration mixtures and pure FLC. The values of electro-optical parameters (i.e. Ps and γ□) were matched the dielectric findings strongly as observed by them. Also the bias voltage required for helix unwinding was depending upon the concentration of guest dye in host liquid crystal was reported.

Dielectric properties of ferroelectric liquid crystalline mixture FLC-6980 and its anthraquinone dye (2% wt/wt) dispersed sample was reported by Raina.et al. [23] in SmC* and SmA phases in the frequency range from 100 Hz to 1 MHz in planar and homeotropic aligned cells. They observed the molecular relaxation mode in the homeotropically aligned cell at 33^0C at a frequency of 36 kHz in the SmC*phase. Also goldstone and a new relaxation mode were observed in the planar cells. A soft mode was appeared in the vicinity of the SmC*–SmA transition. The dielectric increment, distribution parameter and relaxation frequency of these modes were reported at different temperatures and bias voltages.

Srivastava.et al. [21] reported the dielectric relaxation behaviour of a ferroelectric liquid crystal mixture CS-1016 with and without doping of anthraquinone dye at a concentration

of about 5% wt/wt ratio in the LC mixture. The dielectric properties of dye dispersed and pure ferroelectric liquid crystal mixture were reported as a function of temperature and frequency. They observed the goldstone mode in SmC* phase, while soft mode in SmA phase and proved their existence with the help of Cole–Cole function. Also they were reported that the addition of dye strengthens the helix in SmC*phase, shown by higher relaxation frequency and dielectric strength observed by them in the dye dispersed ferroelectric liquid crystal mixture. The SmC*–SmA phase transition point became sharper with the addition of dye in ferroelectric liquid crystal material and also shifted towards lower temperature side was observed by them.

In order to study the shifting of phase transition temperature of ferroelectric liquid crystals due to addition of dye molecules, Shukla.et al. [16] used two ferroelectric liquid crystal materials (Felix 16/030 and Felix 16/100) and their five mixtures with anthraquinone dye (1%, 2%, 3%, 4% and 5% wt/wt). The phase transition schemes were reported from the optical transmittance and the dielectric permittivity study with variation of temperature in the range of 30 to 100^0C. They observed that both the samples showed the shifting of phase transition temperature with dye concentration, especially the SmC*–SmA phase transition temperature and the SmC*–SmA phase transition phenomenon became stronger with the addition of dye molecules. A theoretical explanation for shifting of phase transition temperature was also given by them. They found that the amount of shift in transition temperature agrees both from optical and dielectric studies.

1.12 Aim of the thesis

The main objective of the present thesis was to understand the influence of antraquinone dye on pure FLC systems. Morphological, dielectric and electroptical data were the various tools used to study the behaviour of FLCs on dye addition. The present work shows how the presence of dye changes the dielectric properties of the FLCs due to the strong interaction between FLC and dye molecules. Thus, we concentrate on the impact of antraquinone dye on the dielectric and morphological properties of FLC systems.

Chapter-2

Experimental Techniques

This Chapter gives you an overview about the preparation of liquid crystal cell and the characterisation techniques used for the morphological and dielectric investigations.

2.1 Materials

The materials studied in present work is commercially available ferroelectric liquid crystal material named SCE9 , were purchased from Merck Ltd.(U.K.) and used without further purification. The observed phase sequence is:

$$\text{SmC}^* \xrightarrow{70^0\text{C}} \text{SmA} \xrightarrow{100^0\text{C}} \text{N}^* \xrightarrow{129^0\text{C}} \text{Isotropic} \qquad \text{(SCE9)}$$

The dye used is antraquinone blue dye named as B2 which has 100% solubility in liquid crystal. The molecular structure of anthraquinone dye is shown in fig. 2.1.

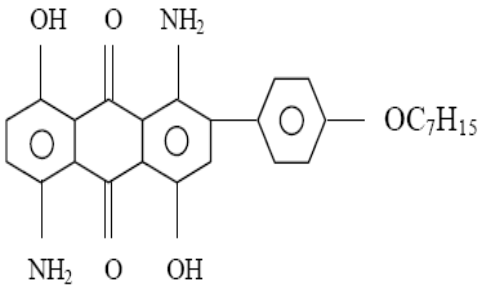


Fig.2.1: Molecular structure of the anthraquinone dye used in present work

2.2 Fabrication of liquid crystal cells

In order to understand and explore the properties of liquid crystals, one of the most significant steps is the preparation of sample cells which acts as a base for whole characterization process. The procedure for cell fabrication can be divided into the following steps:

1. Deposition of a transparent conducting coating (ITO) on glass plates.
2. Surface treatment for alignment of LC material.

3. Cell assembly, filling the cell with appropriate LC material and sealing with optical adhesive polymer.

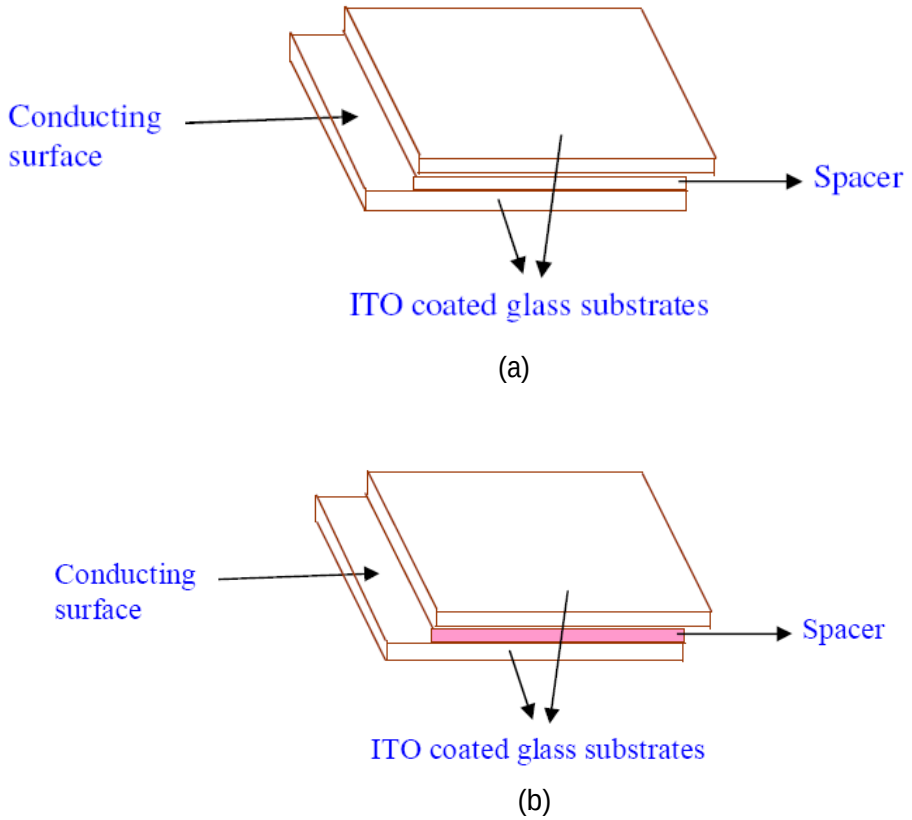


Fig. 2.2 An assembled (a) empty (b) filled liquid crystal cells

Pure (FLC) and antraquinone dye dispersed ferroelectric liquid crystal mixture cells were prepared using conducting indium tin oxide (ITO) coated glass substrates. The transparent and highly conducting indium tin oxide (ITO) coated optically flat glass substrate were used as electrode, which allows one to control the optical alignment of the LCs molecules and also to study the dielectric relaxation processes. Figure2.2 shows an assembled empty and filled liquid crystal cells. The substrates were initially washed with soap solution, rinsed with acetone (purity 99.9%), distilled water and then dried in a vacuum chamber. These substrates were then put in dust free (laminar flow) chamber to ensure proper cleaning conditions. Dust free (laminar flow) chamber for liquid crystal cell preparation is shown in figure 2.3.

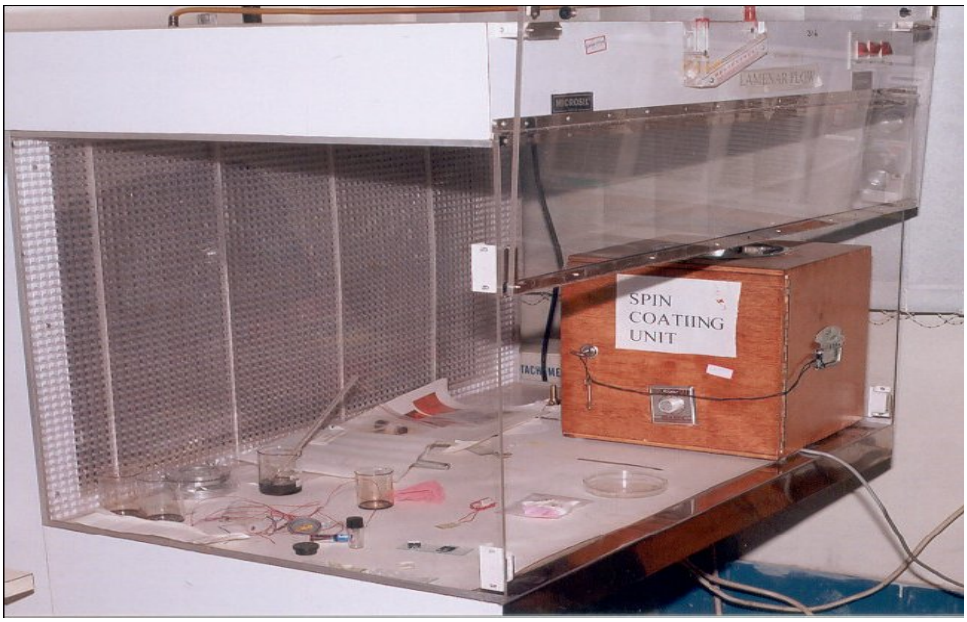


Fig. 2.3: Dust free (laminar flow) chamber for liquid crystal cell preparation.

Alignment

Alignment of the liquid crystal molecules is the most important step in the fabrication of sample cells. The molecular alignment is believed to depend on the competition between the surface tension of liquid crystal and substrate. Different alignments are used according to the requirement in display devices. Out of the two basic forms of alignment for liquid crystalline compounds or mixtures i.e. the homeotropic and homogenous, we used homogenous alignment method.

Homogeneous alignment

In this method constituents molecules of LC are oriented parallel to the supporting substrates. In order to obtain homogeneous alignment, unidirectional rubbing is necessary.

Rubbed polyimide

The homogeneous sample is prepared using polymer (Nylon 6/6) coated rubbed substrates. First of all, the polymer (Nylon 6/6) solution is spin coated (1400rpm) on the glass substrates. The excess solvent was evaporated by keeping the sample at 120 ^{o} C for 1 hour in the vacuum oven. Finally, the polymer treated substrates were rubbed unidirectionally with a good quality velvet cloth.

Assembling, Sealing and Filling the Cell

Assembling of the cell

After the alignment and rubbing process, the glass substrates are to be assembled to form a cell. The conducting sides of these ITO coated glass substrates were joined together and separation between the substrates was maintained with the help of mylar spacer of known thickness.

Sealing the cell

Finally the assembled glass plates were sealed with optical adhesive (UV curable polymer) fevitite at the two corners, and then cured the cell in presence of UV light. The electrodes were connected at the ITO coated substrate surface of the cell using indium (metal) ingot to obtaining better contact.

Filling the cell

The liquid crystal material is placed between the small opening between the two plates and by means of capillary action it is filled into the cell at its isotropic temperature and then cooling the cell slowly from isotropic phase to room temperature. The complete structure of the sample cell is given in fig 2.4

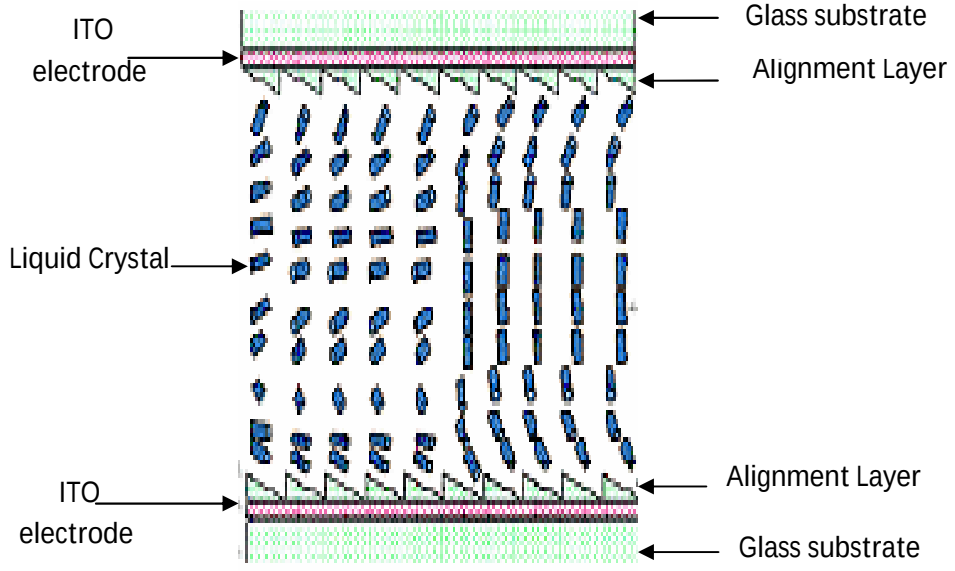


Fig2.4: Structure of liquid crystal sample cell used in the experiments

(i) (ii) (iii)

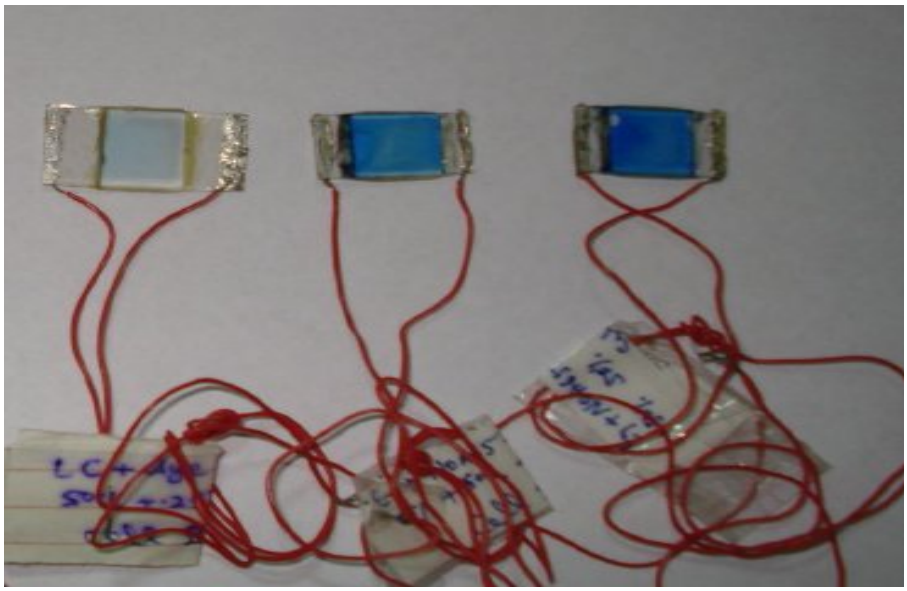


Fig.2.5: Filled DDFLC sample cells with varying concentration of anthraquinone blue dye (i) 0.5wt% (ii) 1.0wt% (iii) 2.0wt%

2.3 Preparation of Dye dispersed ferroelectric liquid crystal samples

In this study, we prepared five samples; one is pure FLC and other at various concentration of dye 0.1, 0.5, 1.0 and 2.0 wt% respectively. Liquid crystal mixture and dye content is taken in wt to wt% in a glass vial. The reaction mixture was heated up to the isotropic temperature of the LC material and cooled to room temperature to make the homogenous distribution of dye molecule. The homogenous mixture is filled in the assembled cell by the capillary action by placing the cell on hot plate maintained at the isotropic temperature of FLC and then allowed to cool down to room temperature. Finally, the filled cell sealed with optical adhesive and contact made with indium solder. The complete methodology of samples preparation is shown in figure 2.6 in the form of flow chart. The prepared dye dispersed FLC sample cells are shown in fig2.5. The same procedure was employed for all the reaction mixtures of different concentration of dyes in order to make valid comparison with the results from the dye dispersed FLC mixture. After sealing and curing, the samples were placed in a linkam temperature programmer cum hot stage. Further various characterizations such as thermal, optical and dielectric behavior of the prepared sample were investigated by using polarizing microscope, LCR meter setup.

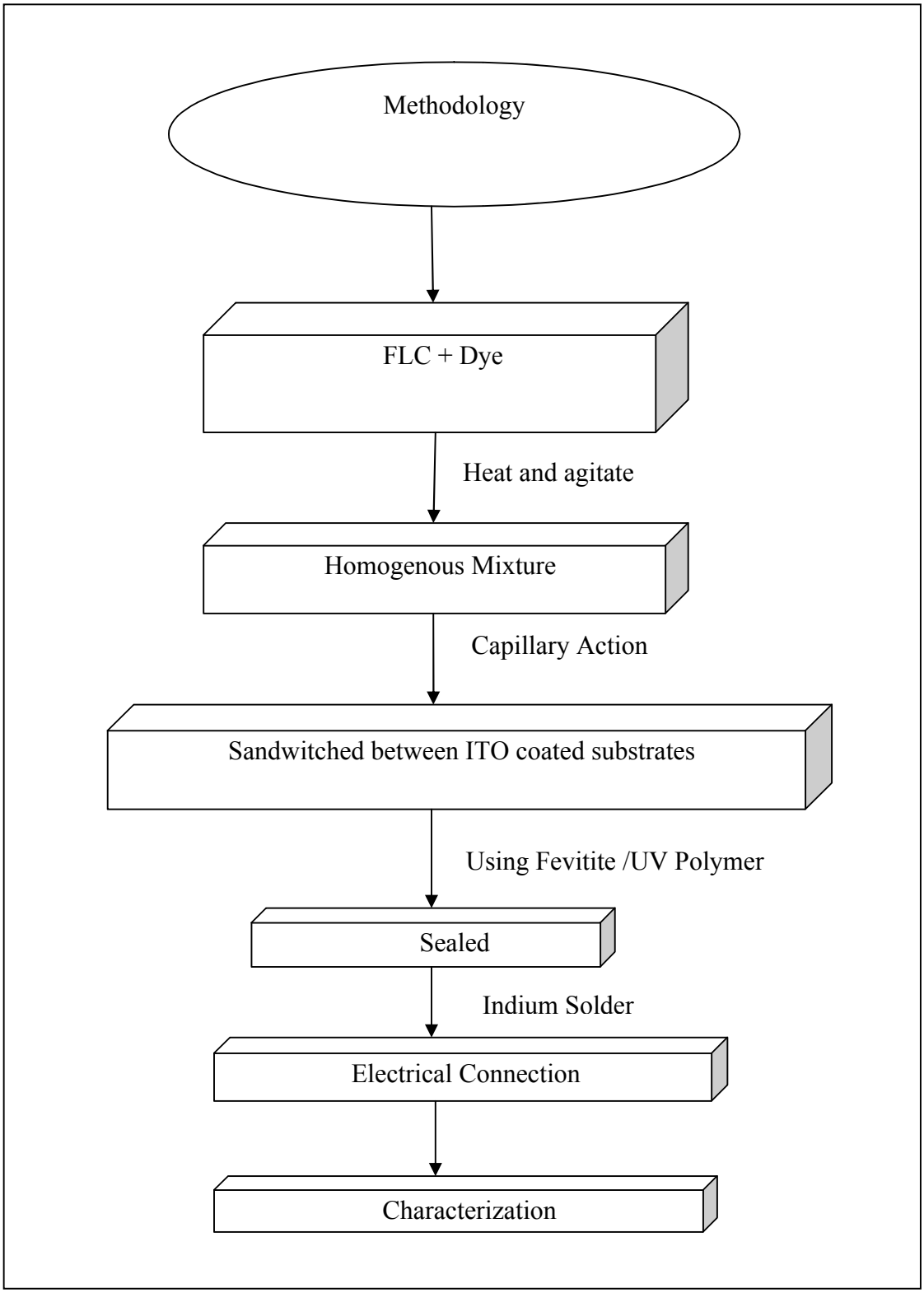


Fig2.5: A flow chart for the preparation of dye dispersed ferroelectric liquid crystal samples.

2.4 Characterization Techniques Used

The characterization of the liquid crystal sample cell is performed by dielectric studies and texture investigation. Following characterization for desired experiments were used.

2.4.1 Morphological Characterization by Polarization microscopy

2.4.1.1 Optical polarizing microscopy

The optical studies observed in ferroelectric liquid crystal and antraquinone dye doped ferroelectric liquid crystals investigated using an Olympus optical polarizing microscope (Model BX51P) at a magnification of 10X under crossed polarizer using long working distance objective lens. The optical micro-textures of LC materials were also investigated as a function of temperature other physical parameters. A block diagram of our experimental set-up for the investigation of optical textures, dielectric studies and other parameters of liquid crystal is shown in Fig.2.7.

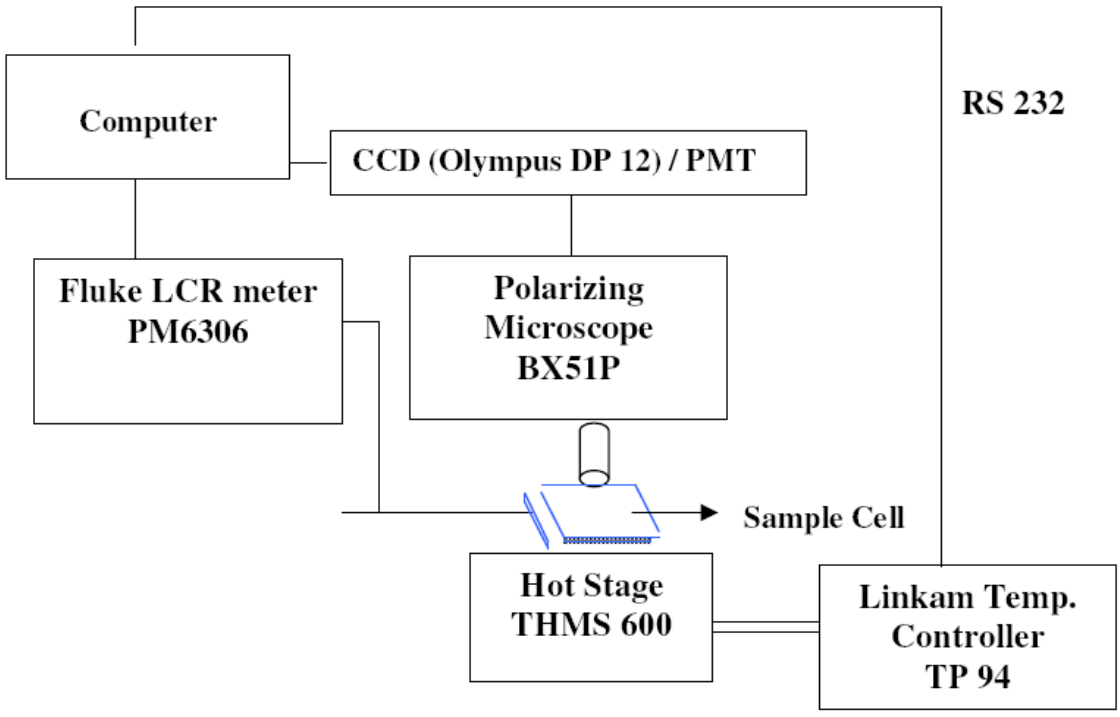


Fig. 2.7: Block diagram of the experimental set-up to study the morphological and dielectric studies of dye doped Ferroelectric mixture.

2.4.1.2 Temperature programmer along with hot stage

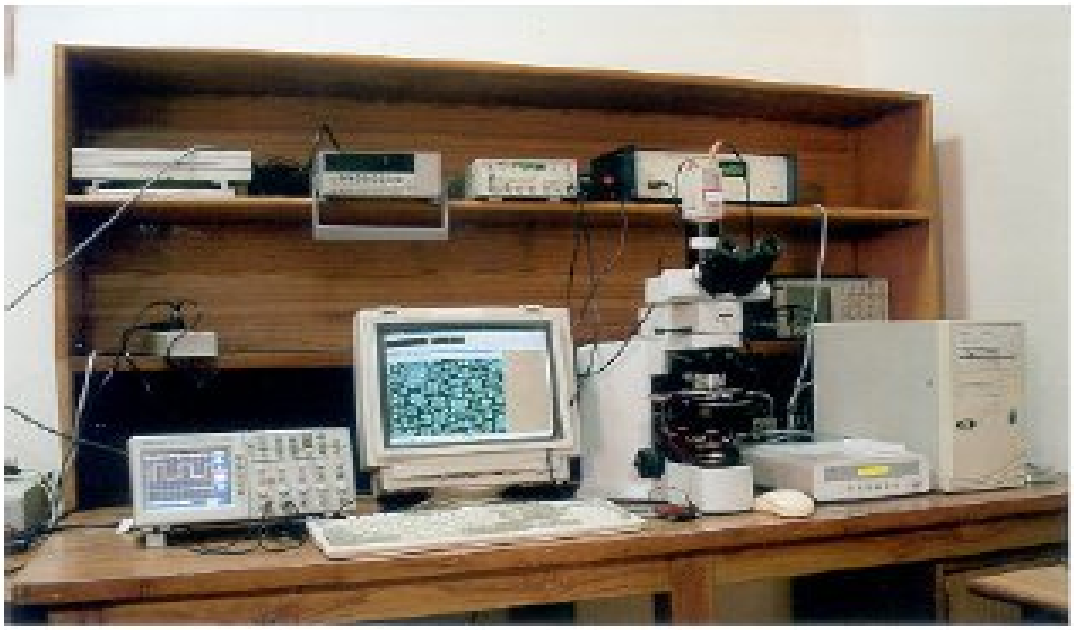


Fig. 2.8: Experimental set-up in the lab to study the morphological and dielectric studies of dye doped Ferroelectric mixture.

Thermal polarizing microscopy studies were investigated using Linkam temperature programmer TP94 and hot stage THMS 600. The TP94 is specifically designed for precise temperature control of the Linkam heating/freezing stages. The stage sensor is digitally linearized to give accurate temperature readout, the controls and their functions have been carefully chosen for simple and easy operation. The temperature range is –196 ^{0}C to 600 ^{0}C. Heating or cooling rates can be changed almost instantly using the three rate keys. The heat ranges are from 0.1 to 0.9^{0}C/min at 0.1 degree intervals from 1.0 to 9.0 ^{0}C/min at 1.0 degree intervals and from 10 to 90^{0}C degree intervals. A varying dc signal is used to control the stage and results in an even application of power, which avoids the bursts seen with conventional burst fire ac techniques. An optional remote control gives single key control of three programmable heating/cooling rates and the HEAT, COOL and HOLD functions. The three programmable heating/cooling rates are held in memory when power is switched off. The temperature and limit values can also be

stored and recalled using the remote control facility. The complete experimental set-up to study morphological properties is also shown in fig. 2.8.

2.4.2 Dielectric measurements using RCL meter

The dielectric measurements were carried out using a programmable automatic RCL meter (FLUKE PM 6306) in the frequency range 50Hz to 1MHz. The cell was calibrated using air and benzene as standard references. The frequency and bias dependence of the real and imaginary parts of the complex dielectric permittivity have been studied in detailed at room temperature. The dielectric properties of the Dye doped FLC were made in the presence of applied voltages that produced alignment (and, therefore, optical switching) of the LC phase. Measurement in the high frequency range has been limited to 1 MHz because of the dominating effect of finite resistance of ITO coating on glass plates and lead inductance.

Fig. 2.9: Programmable automatic RCL meter [FLUKE PM6306] used for dielectric studies.

2.4.3 Spontaneous Polarization and Rotational Viscosity

We used Automatic Liquid crystal Tester (ALCT3, Instec, U.S.A.) (fig2.10) interfaced with the computer via Win LC software shown in fig. 2.11. In present study, a triangular wave pulse was used to estimate the value of $P_{s.}$

Fig2.10: ALCT meter used to study the value of Ps and viscosity.

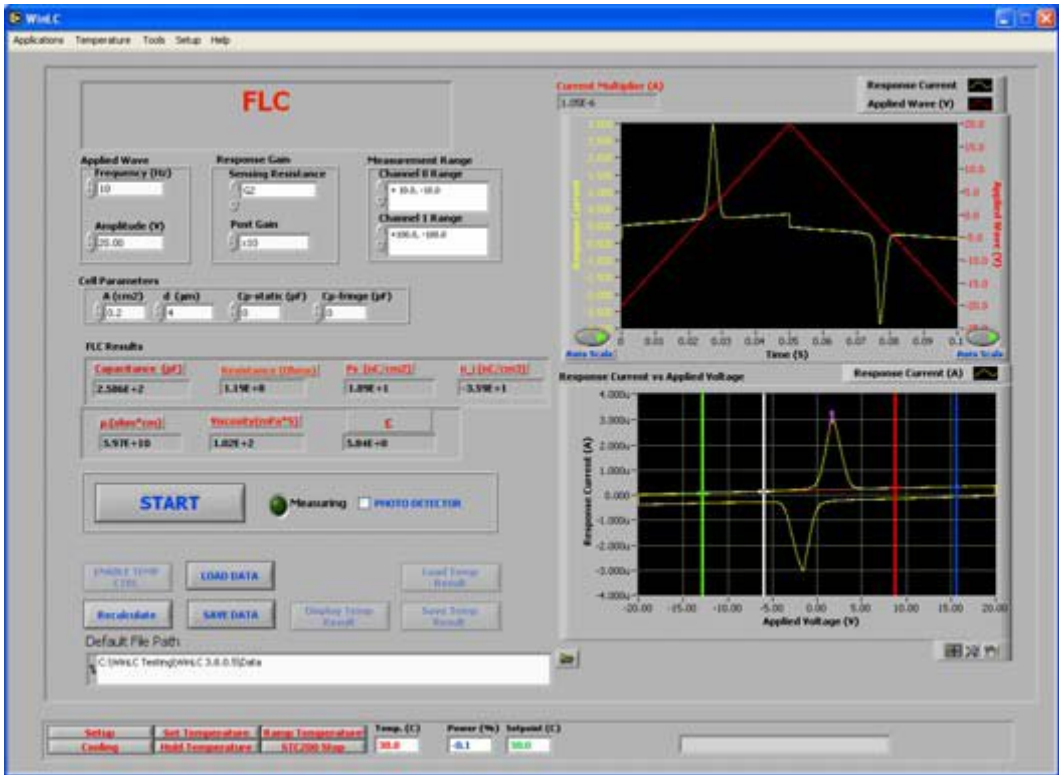


Fig2.11: Software Interface for FLC Polarization Measurement

The FLC material sandwiched between two conductors can be represented schematically by a parallel combination of a resistor (R), a capacitor (C) and a polarization realignment device (P). Current I (t) induced in the ferroelectric LC material by applying a voltage

V(t) can be written as a sum of the following three contributions: Ionic current $I_{R,}$ charge accumulation in the capacitor (displacement current) I_c and polarization realignment current $I_{p.}$ Thus one obtains

$$I(t) = I_R + I_c + I_p$$

$$= V(t)/R + C\, dV(t)/dt + dP/dt$$

where P is the amount of charge induced by polarization reversal in the cell on application of an electric field. By selecting a suitable value of resistance R (about two orders of magnitude smaller than that of FLC sample resistance) we can get suitable overall current profile to subtract the ionic and capacitive currents by drawing a baseline.

Chapter - 3

Results and discussion

Dielectric studies of FLC materials have been of increasing interest in the past few years, both theoretically as well as experimentally. The dielectric response below 1MHz mainly consists of two modes in FLCs .These are mainly related with director fluctuations in the form of azimuthal angle fluctuation, i.e., Goldstone mode and tilt angle fluctuation, i.e., soft mode. In SmC* phase Goldstone mode predominates over the soft mode and soft mode comes into existence near the SmC*–SmA phase transition temperature. When dye molecules have been introduced into the pure FLCs, their molecular properties changes drastically. Addition of dye molecule into the pure FLC mixture results in redistribution of intermolecular interaction energies. This redistribution of interaction energies will bring some change in molecular geometry and intermolecular interactions. Therefore, dielectric relaxation spectroscopy is one of the important tools to study the changes induced in molecular properties of the FLCs. Estimation of rotational viscosity and spontaneous polarization of dyed FLCs by polarization reversal current method help in better understanding the effect of dye molecules on dielectric properties of pure FLCs. The phase sequence of Ferroelectric liquid crystal mixture (SCE9) and dye doped FLC mixtures was noted through thermal polarizing microscopy and shown in the following table3.1.

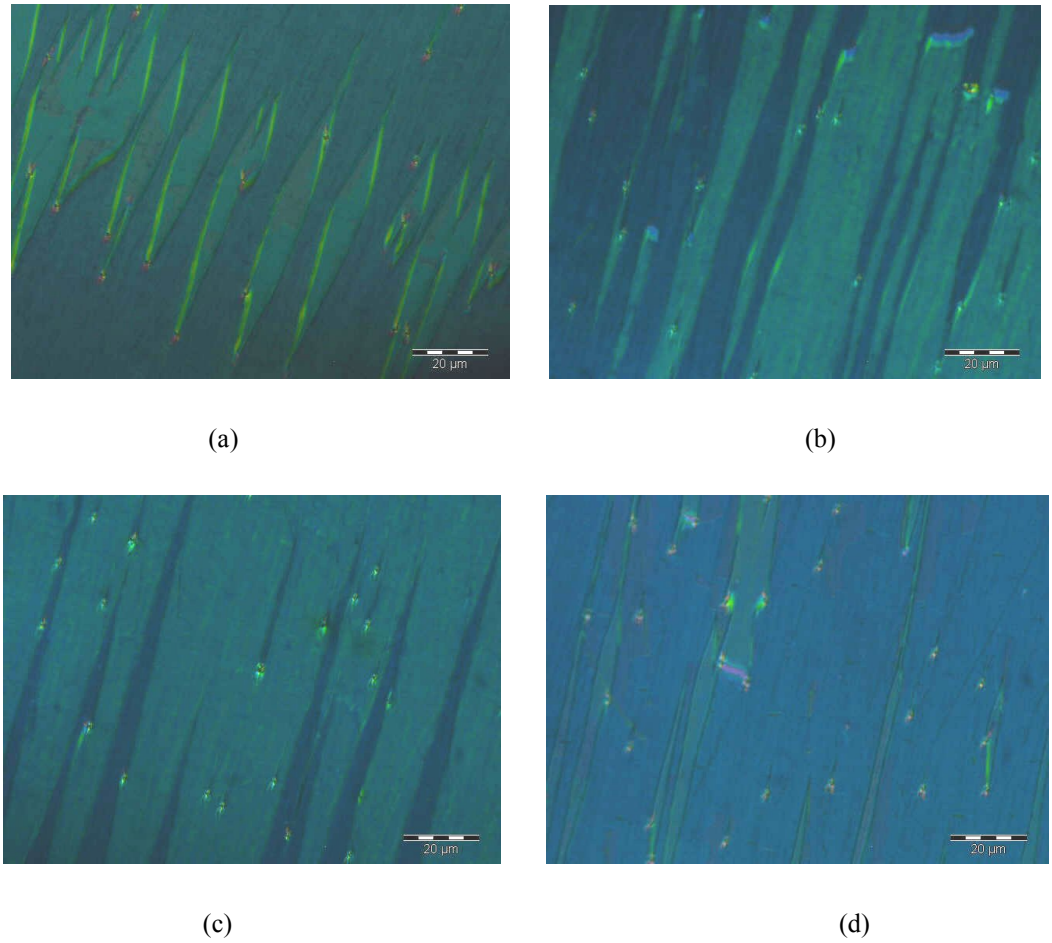
Table3.1: Phase Sequence of FLCs and Dye doped FLC in ^{0}C

Sample	**Crystal**	**SmC***	**SmA**	**N***	**Isotropic**
SCE9	Unknown	-20*	70	100	129.0
0.1wt%Dye	Unknown	-20 *	70	100	128.5
0.5wt%Dye	Unknown	-20 *	68	99	127.0
1.0wt%Dye	Unknown	-20 *	65	98	126.4
2.0wt%Dye	Unknown	-20 *	55	96	124.0

***** could not be measured due to experimental limitation.

3.1 Morphological studies of antraquinone dye dispersed SCE9

Textures are the patterns which are observed microscopically on liquid crystalline samples, usually in polarized light. Change in texture at a particular temperature indicates the occurrence of phase transition. Fig 3.1 shows micrographs of a pure, 0.1, 0.5, 1.0 and 2.0 wt% antraquinone dye dispersed FLC (SCE9) obtained under crossed polarizers in SmC* phase.



(a) (b)

(c) (d)

Fig 3.1 : Micrographs at 10X of (a) pure (b) 0.5 (c) 1.0 (d) 2.0wt% antraquinone dye dispersed SCE9 obtained under crossed polarizers in SmC* phase.

Texture studies show a change, which is clear from the comparison of the textures of dye doped and pure FLC. From texture studies it was observed that only physical interaction takes place between the molecules of dye and pure ferroelectric liquid crystal mixture. No

significant change was observed with dye in any concentration but only the change in color was observed (fig. 3.1). The dye dispersed samples shows blue color.

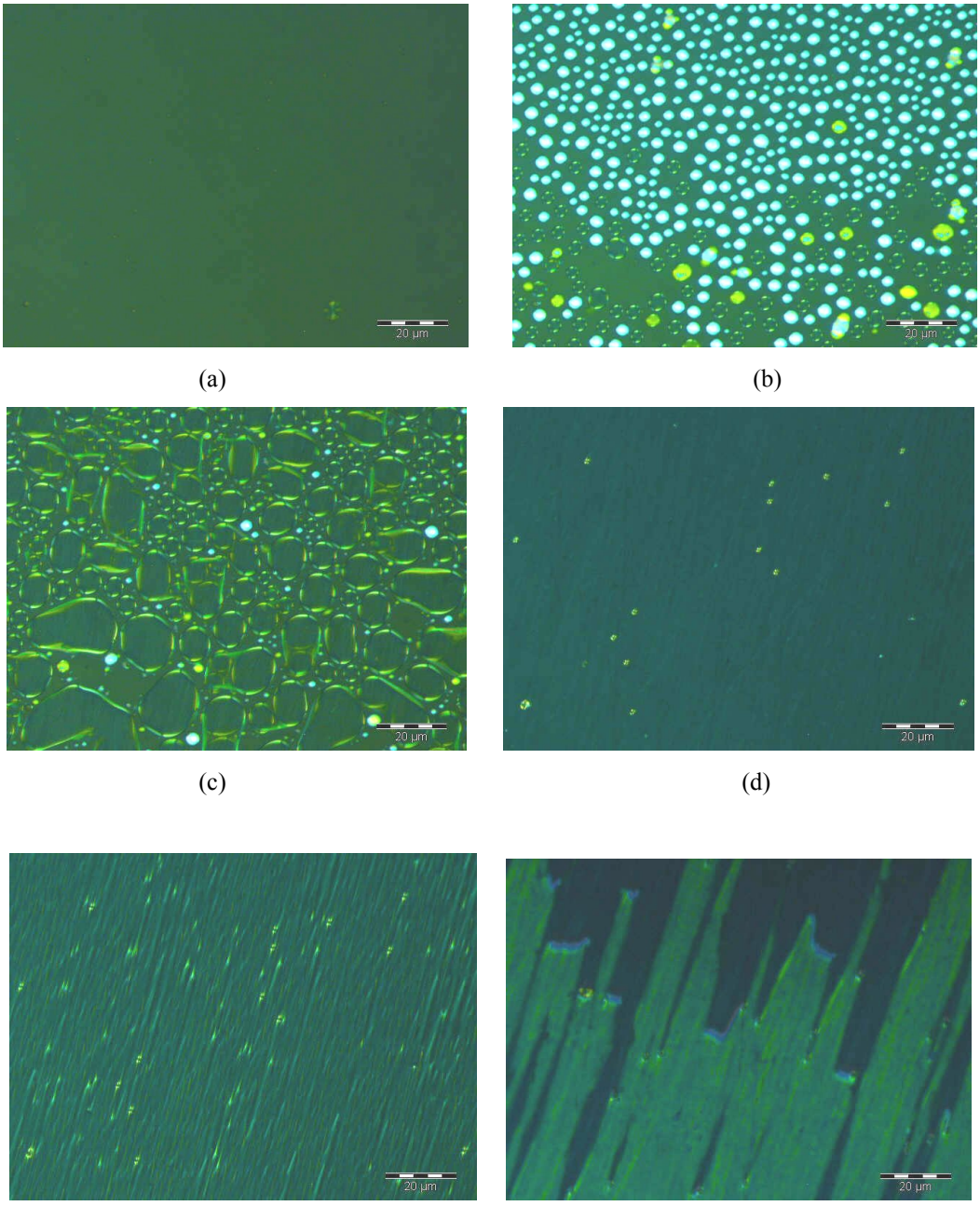


Fig. 3.2: Micrographs at 10X showing structural evolution of 1.0 wt% Dye doped SCE9 during cooling from isotropic to room temperature.

The textures observed under cooling condition are shown in fig3.2 (a). At 126.4^{0}C, the sample was dark under crossed polarizer, suggesting that the DFLC mixture is in the isotropic state. The nucleation starts at126^{0}C (b) and corresponds to nucleation growth at 125^{0}C (c) which transform to cholestric phase at 123^{0}C (d).The cholesteric structure shows uniform texture with color depending on the pitch .Moreover, the irregularities in the cholesteric LC cell can provoke the appearance of defects called oily streaks. Fig (e) shows SmA phase at 98^{0}C.Our textural study confirms that the Smectic A – Smectic C* transition temperature of the mixed dyed FLC is located about 65ºC. The presence of ferroelectric domains features the SmC* phase.

3.2 Dielectric spectroscopy

3.2.1 Temperature dependence of dielectric permittivity (ε')

Temperature dependence of dielectric permittivity of pure and dye doped FLC mixture at the frequency 100 Hz has been shown in figure 3.3.

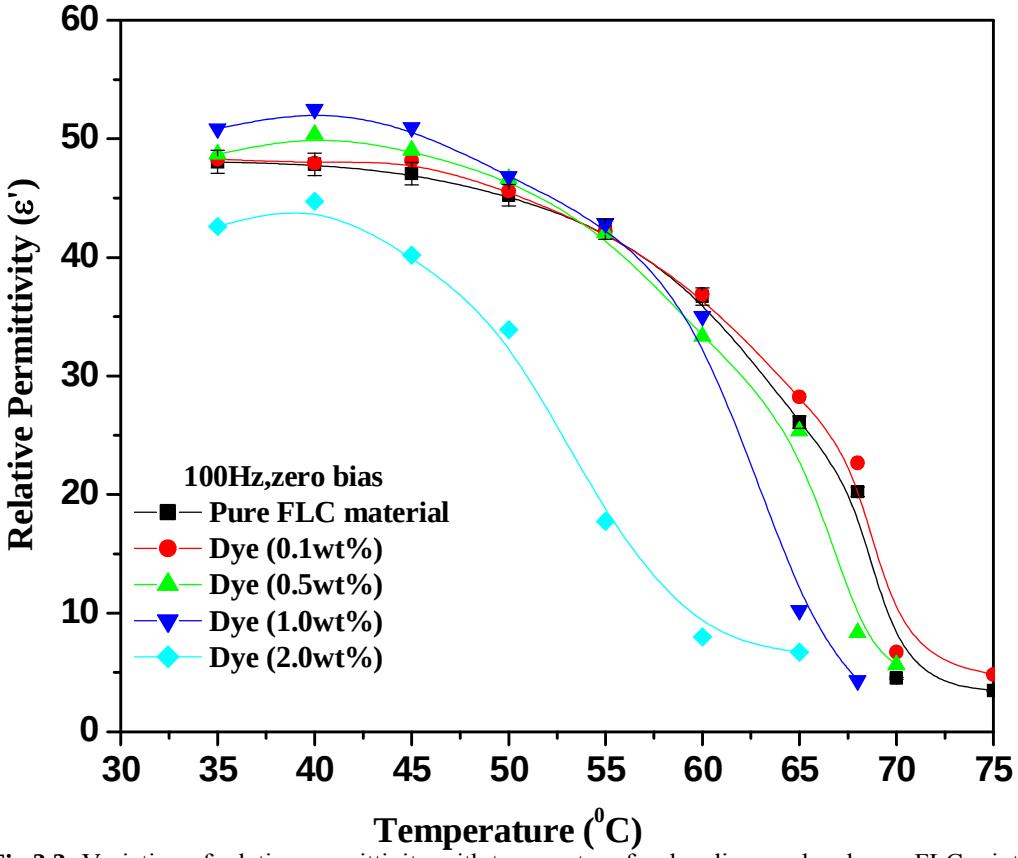


Fig 3.3: Variation of relative permittivity with temperature for dye dispersed and pure FLC mixtures

For pure ferroelectric liquid crystal material, the dielectric constant increases with the increase in temperature and shows a maxima as shown in Fig3.3 (47.95 for pure), which is related to the maximum strength of the helix in SmC* phase.After that dielectric permittivity decreases slightly with increase in temperature for SmC* phase and show a sharp decrement near the SmC*–SmA phase transition temperature. This abrupt fall in the value of relative permittivity is because of helix unwinding near this transition temperature after maximum strength of helix in SmC*phase and helix disappears as sample goes into SmA phase.

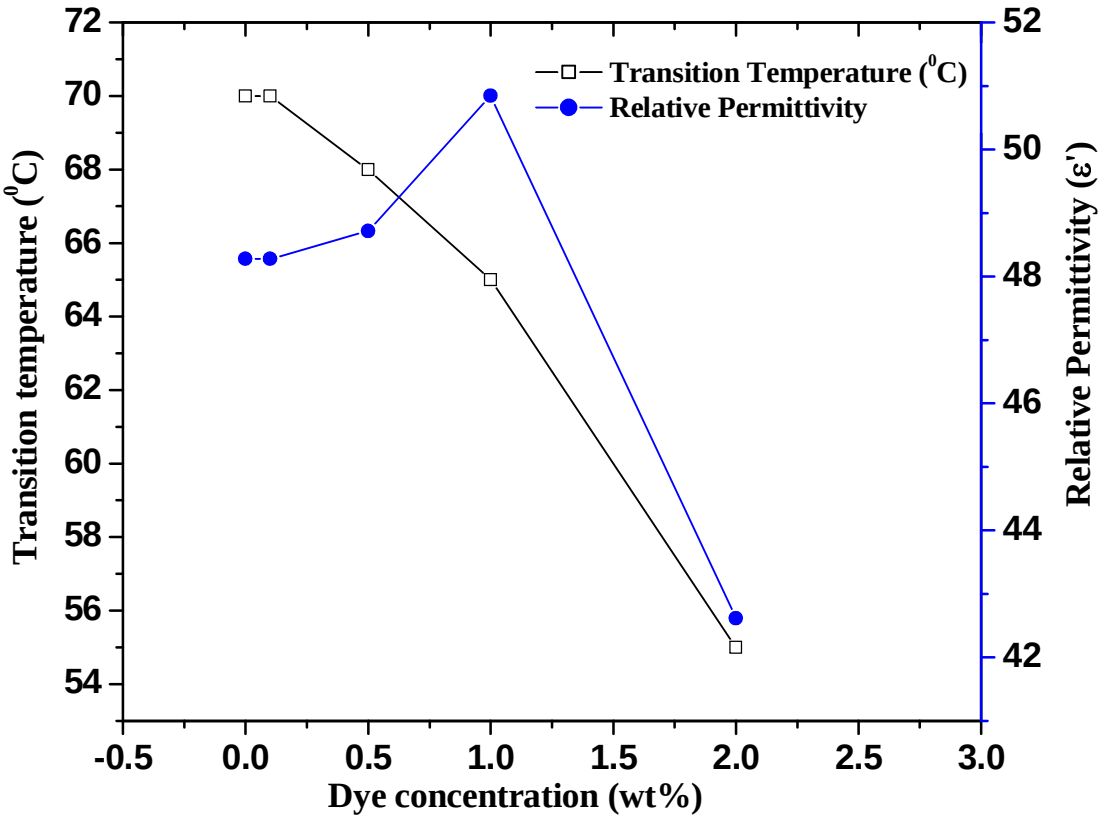


Fig 3.4: Variation of SmC*–SmA phase transition temperature and relative permittivity with respect to the dye concentration in pure FLC system

Similar temperature dependence has also been observed for dye doped FLC mixtures. Trend of relative permittivity for the dye doped FLC is also similar to the pure FLC material but the magnitude of relative permittivity change as compared to their pure FLCs counterparts (table3.2). The value of relative permittivity were found to increase slightly

for mixtures having lesser concentration of dye i.e. for 0.1wt%, 0.5wt% and1.0wt%, whereas opposite behavior i.e. decrease has been observed for mixture of the higher concentration of dye (i.e. 2.0wt %) into pure FLC mixture (see table3.2).

Table 3.2: Variation in transition temperature and relative permittivity in FLC material by addition of dye at various concentrations.

Dye Concentration (wt %)	**Pure**	**0.1**	**0.5**	**1.0**	**2.0**
T_c (^{0}C)	70	70	68	65	55
Relative Permittivity	48.27	48.27	48.71	50.85	42.62

The value of relative permittivity were found to increase slightly for mixtures having lesser concentration of dye i.e. for 0.1wt%, 0.5wt% and1.0wt%, whereas opposite behavior i.e. decrease has been observed for mixture of the higher concentration of dye (i.e. 2.0wt %) into pure FLC mixture (see table3.2).From Fig.3.3 it reveals that the SmC*–SmA phase transition temperature decreases as we increase the concentration of the dye in pure FLC matrix. The plot between the SmC*–SmA phase transition temperature and relative permittivity in response with the concentration of dye molecule is shown in fig. 3.4. Figure itself shows that change in the transition temperature follows almost a straight line. Not only phase transition shift towards lower temperature side but also the phase transition phenomenon becomes sharper (i.e. the breadth of SmC*–SmA phase transition is reduced after addition of dye in pure FLC). This sharpness of SmC*–SmA phase transition increases with the increasing concentration of dye molecule in pure FLC mixture.

Whenever dye (like antraquinone) molecules are introduced into the pure FLC mixture they try to fit in the geometry of the host molecules, which strengthen the helix of the mixture. Moreover the dipole moment of dye molecule contributes to the dipole moment of pure ferroelectric liquid crystal molecule and thus results in increase in the relative permittivity with addition of a dye at lesser concentration (0.1wt%,0.5wt%,1.0wt%). This supportive nature of dipole moment not only increases the dielectric constant of the system but also strengthen the helix of ferroelectric liquid crystal sample in SmC* phase

may be due to this pre-transition phenomenon reduces after the addition of dye. This nature of helix strengthening has been confirmed by bias electric field study of the dielectric permittivity as discussed later (fig 3.8).

At higher concentration of dye (2.0wt %) in pure FLC, excessive dye hinders the formation of ferroelectric domains and consequently the decrease in the value of relative permittivity has been observed in this case. The variation in relative permittivity of dye doped FLCs with any concentration of dye suggest that after a certain percentage of dye in FLC, the increasing trend of relative permittivity is saturated and dielectric properties cannot be enhanced. This concentration is dependent on the interaction of dye and FLC molecules and is different for different dye concentration of FLC systems. It is termed as saturation concentration for a particular guest host system. In our case, saturation concentration is 1.0wt%.

A theoretical approach of shifting of transition temperature for dye doped FLC mixture is discussed in Chapter 1. According to theoretical approach, the SmC*-SmA phase transition temperature of dye doped system (Tcd*) in the terms of SmC*-SmA phase transition temperature of pure FLC mixture (Tc*) is as given below:

$$Tcd^* = Tc^* - \lambda x/\alpha \qquad (1)$$

Here x is the concentration of dye in the FLC mixture, λ is coefficient of dye concentration, while α is mean field coefficient. According to equation (1) the value of λ should be positive for present dye and FLC mixture as the SmC* to SmA transition temperature is decreased after the addition of dye. The temperature at which the relative permittivity stabilizes has been taken as the transition temperature of SmC* to SmA transition.

The temperature dependence of dielectric permittivity ε' at different frequencies is shown in Fig 3.5. It was notice that dielectric permittivity attains saturation at about 5 kHz. For all the samples, at higher frequencies (above 5 kHz), no significant variation in the dielectric permittivity was observed but at low frequencies (50Hz, 100Hz) dielectric permittivity value were more predominant.

This behavior was due the fact that at higher frequency, liquid crystal dipoles had not sufficient time to align themselves with the direction of applied electric field. The

dielectric permittivity decreases with temperature as shown in fig. 3.5. At high temperature, the thermal agitation became more dominant over intermolecular interactions which result in collisions between molecules and hence randomization of dipoles. This randomization gives decreased in dielectric permittivity.

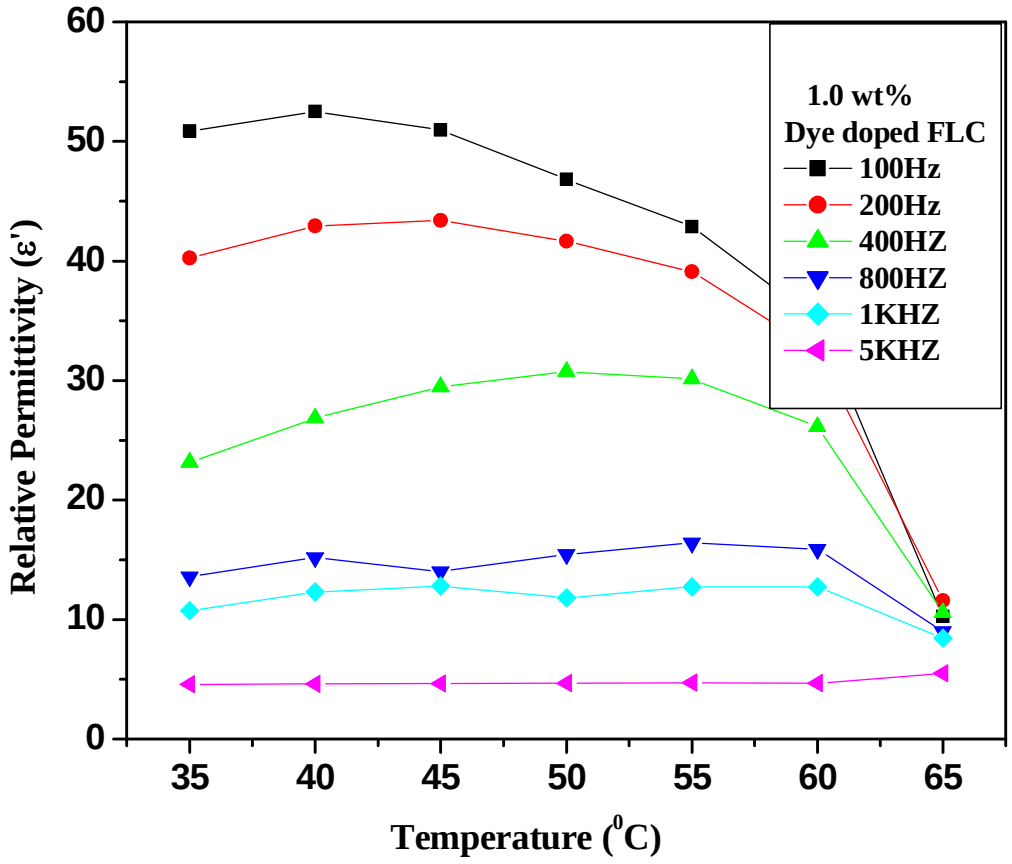


Fig 3.5: Dielectric permittivity as a function of temperature at different frequencies for 1.0 wt% dye doped Mixture

3.2.2 Frequency dependence of dielectric permittivity and dielectric loss (ε', ε")

The relaxation phenonmenon of FLC with a planar alignment is due to the collective dielectric processes such as the Goldstone mode and soft mode. The Goldstone mode dominants over the whole SmC*phase where as Soft mode appears at higher frequencies near SmC*SmA phase transition temperature. The frequency dependence of the real and complex permittivity of pure and dye doped FLCs mixtures in the SmC* are shown in fig 3.6 and fig 3.7 respectively.

From fig. 3.6 it shows that at low frequencies a slight decrease in dielectric permittivity in the SmC* phase has been observed at high concentration of dye (2.0wt%). On the other hand an increase in permittivity results at low concentration of dye (0.1wt%,0.5wt%,1.0wt%) but at higher frequency there was no significant variation in dielectric permittivity values. In FLC, GM is related to the fluctuation of the helix as a whole. The contribution of this mode is maximum when the helix is undistorted. The distortion of helix by any method leads to suppression of the GM contribution and hence decrease in permittivity(at 2.0wt%).As discussed above, dipole moment of dye molecules support the dipole moment of FLC host molecules, hence result in increase in permittivity at low frequencies results with low dye concentration (0.1wt%,0.5wt%,1.0wt%).

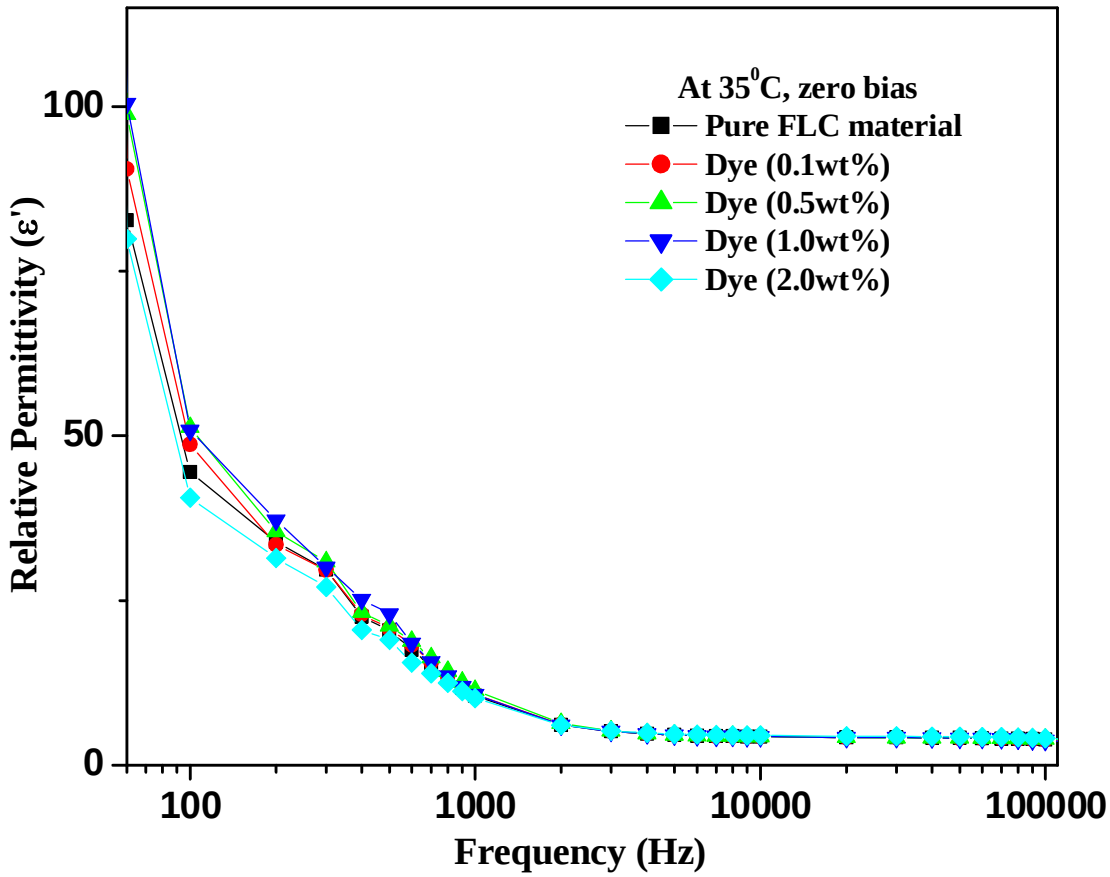


Fig 3.6: Dielectric permittivity (ε') as a function of frequency for pure FLC and Dye doped FLCs at off bias voltage at room temperature.

It was observed that dielectric loss was increased at lesser concentration (0.5wt%, 1wt %) on dispersing dye in ferroelectric liquid crystals at lower frequencies and decrease at high concentration but at higher frequencies there was no significant variation in dielectric loss. The relaxation band of the goldstone mode shifts either towards higher or lower frequency side for dye doped system as compared to pure FLC. The mixture having lesser concentration, the relaxation band shift towards high frequency range and for the concentration above saturation concentration it shifts towards lower frequency region.

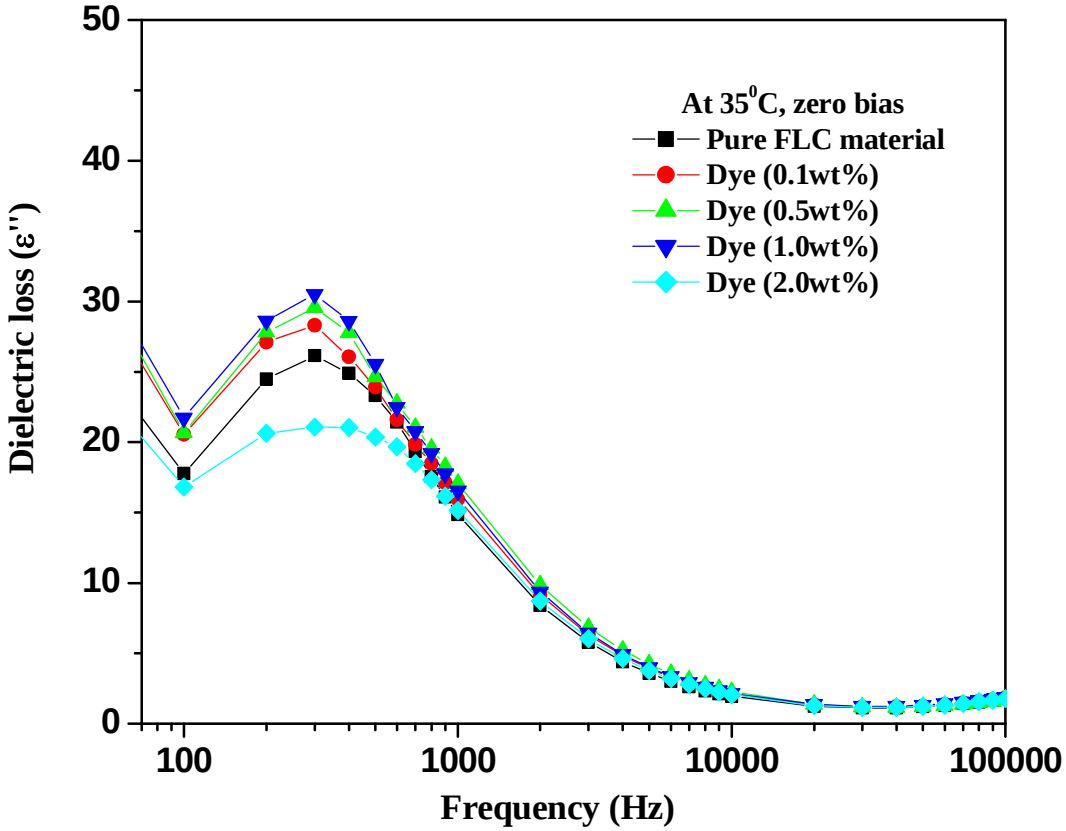


Fig 3.7: Dielectric loss (ε") as a function of frequency for pure FLC and Dye doped FLCs. at zero bias voltage and at room temperature.

3.2.3 Effect of Bias voltage

The pitch of the system will also change with the addition of dye molecule in pure FLC systems which play a major role to understand the guest host effect (dye impact) on FLC system.

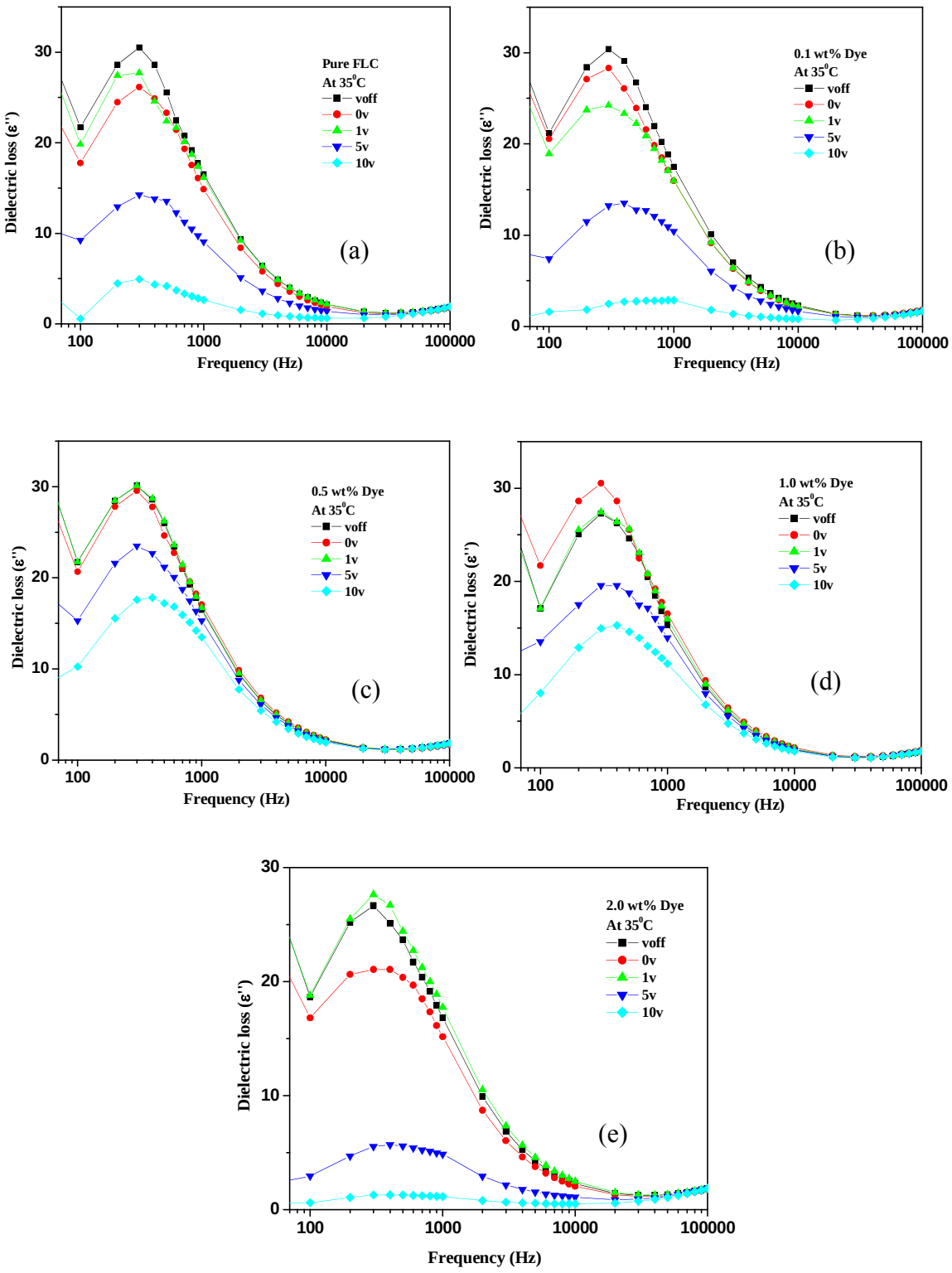


Fig 3.8: Dielectric loss as a function of frequency at different voltage for (a) FLC (b) 0.1% Dye doped FLC (c) 0.5% Dye doped FLC (d) 1% Dye doped FLC (e) 2% Dye doped FLC.

The effect of antraquinone dye on the helical pitch of the pure FLC material has been confirmed by studying the dielectric permittivity as a function of frequency at various bias voltages. The Goldstone mode contribution is suppressed at higher bias voltage.

Absorption curve of pure FLC mixture at various bias voltages is shown in Fig.3.8 (a). It is clear from the figure that the loss was highest without any bias (0V) voltage but decreased with bias voltage e.g. at 10V in the pure and 0.1% dye dispersed FLCs. As the biasing voltage increased, dielectric permittivity and dielectric loss were decreased and reached to minimum values. The dielectric loss values in Goldstone mode are minimum at 10V for pure FLC material. This also indicates that the electric field of 10V is sufficient to unwind the helix structure of this system. The absorption curve to show the effect of bias voltage on all of the dye doped mixtures are shown in Figs.3.8 (b), (c), (d) and (e), respectively. From figure, it indicates that for the dye doped FLC mixture of low concentration (0.5wt%, 1wt %), Goldstone mode suppressed at higher bias voltage (i.e. above 10 V), i.e., to unwind the helix in this system more than 10v field is required. This behaviour predicts that helix of dye doped mixture is stronger than helix of pure FLC material in SmC* phase as the bias voltage required to suppress the Goldstone mode is more for dye doped mixture. On the other hand, for high concentration (i.e.2wt %), to suppress Goldstone mode, we require bias voltage near to pure FLC mixture (around 10v). This type of behavior shows the different kind of contribution of dipole moment of dye molecules to pure FLC mixture at different concentrations.

3.2.4 Relaxation spectra

The dielectric relaxation phenomenon in SmC*phase have been examined using Cole–Cole plots of pure and dye dispersed FLC mixture (fig.3.9). Such distribution of relaxation phenomenon in liquid crystal mixtures results due to the presence of molecules of different sizes. The relaxation process of FLC material results from the combined effect of Goldstone mode and soft mode. The smaller semi- circle in this figure represents the relaxation due to the Soft Mode whereas; bigger semi circle represents the contribution due to Goldstone Mode.

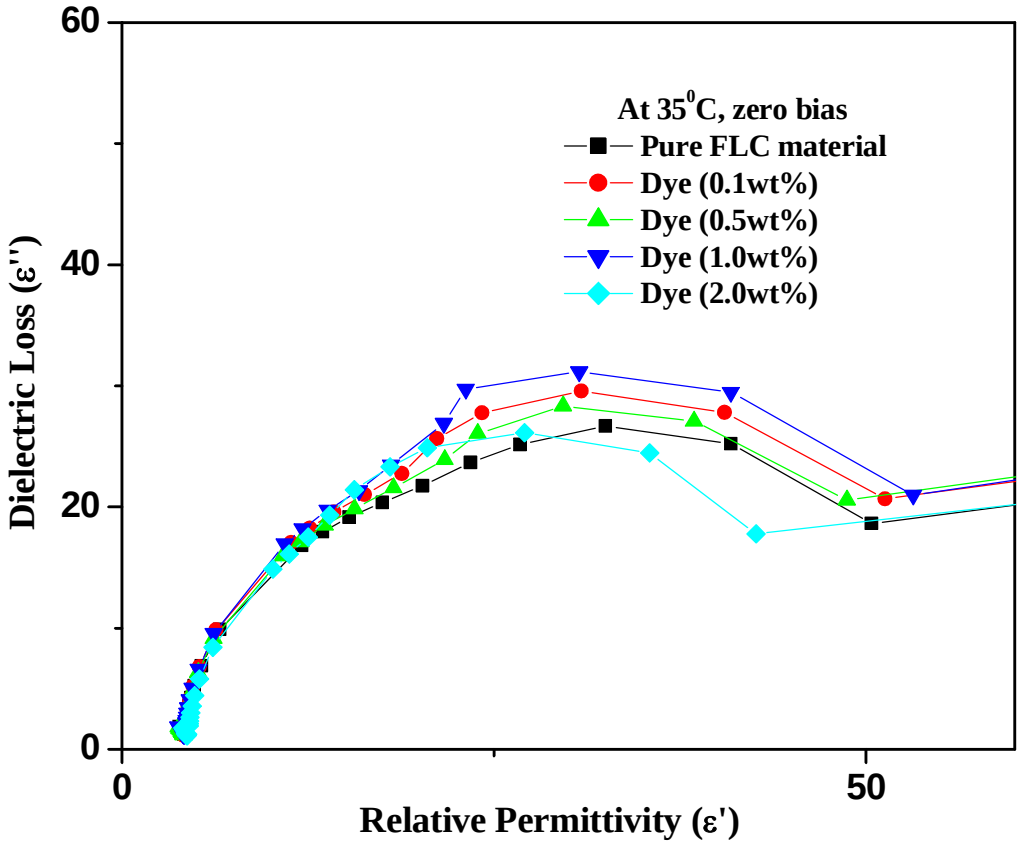


Fig 3.9: Cole-Cole plots for the Goldstone Mode and Soft Mode at different temperature for different mixtures

3.2.5 Temperature dependence of Goldstone mode Relaxation frequency

The trend of relative permittivity curve of dye doped FLC mixture is closely related with relaxation frequency of Goldstone mode. The variation of relaxation frequency with respect to temperature in Goldstone mode for pure and dye dispersed FLC mixtures is shown in fig3.10. As expected from the previous results, relaxation frequency for the lower concentration shifts towards higher frequency side, while for the higher concentration shifts towards the lower frequency side. This opposite behavior of the relaxation frequency is explained with the help of following equation:

$$F_c = \frac{\Gamma K_3}{2\pi} q^2 \qquad (2)$$

Here f_G represents relaxation frequency in Goldstone mode, K_3 is twist elastic constant, q is the wave vector of the helical pitch and Γ is the inverse of the rotational viscosity of the mixture.

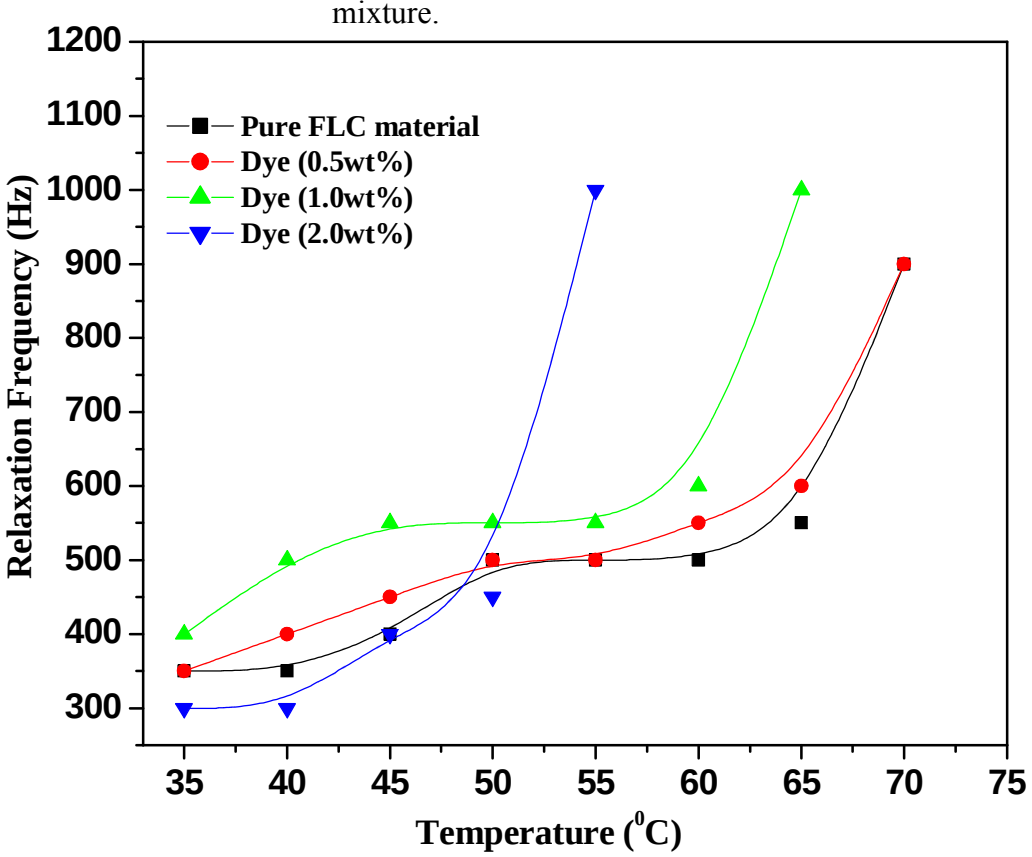


Fig3.10: Variation of Goldstone mode relaxation frequency with temperature for pure and all five dye doped systems at zero bias.

It is clear from the equation (2) that the relaxation frequency is inversely proportional to the rotational viscosity of the system. Addition of dye will alter the rotational viscosity of the system, which results in shifting of relaxation frequency.The increase in relaxation frequency suggests that rotational viscosity is less for mixtures having lower concentration of dye (0.1%, 0.5%, and 1wt %) than the rotational viscosity of pure FLC

and it is on higher side for mixtures with higher concentration of dye(2wt %) The results are graphically shown in the Fig. 3.11 i.e. relaxation frequency with concentration. The decay in rotational viscosity is described by the fact that the effective rotational viscosity in FLC is only due to the Z component of the rotational viscosity as Goldstone mode is due to change in azimuthal angle (Fig 3.12). The Z component of rotational viscosity strongly depends upon the azimuthal angle and this azimuthal angle may alter after the addition of dye in pure liquid crystals matrix. Consequently the rotational viscosity may decrease or increase as observed (Fig. 3.13). For the low concentration of dye, the dipole moment of dye couple with the dipole moment of molecule with the FLC molecules while for the higher dye dispersed mixture (i.e. 2wt%), dye molecule will obstruct the motion of FLC molecule as a result of which rotational viscosity increases. Such behavior results in decrease in the Goldstone mode relaxation frequency of the material. The variation of rotational viscosity with bias voltage is shown in Fig3.13

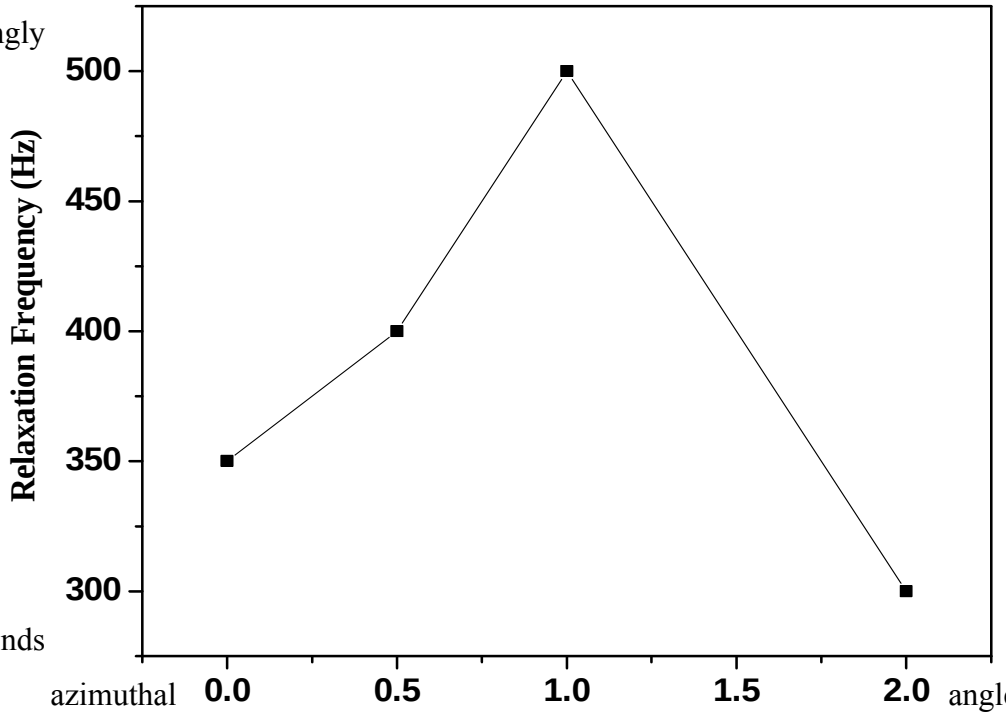


Fig 3.11: Variation of relaxation frequency with concentration of dye in pure FLC.

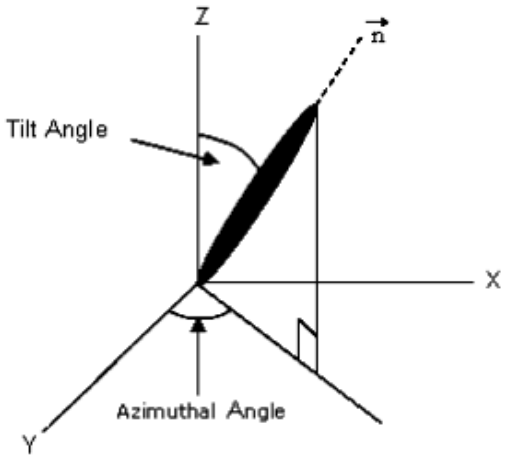


Fig 3.12: Schematic diagram of the molecular arrangement of FLCs. Here, XY plane is presenting the Smectic layer.

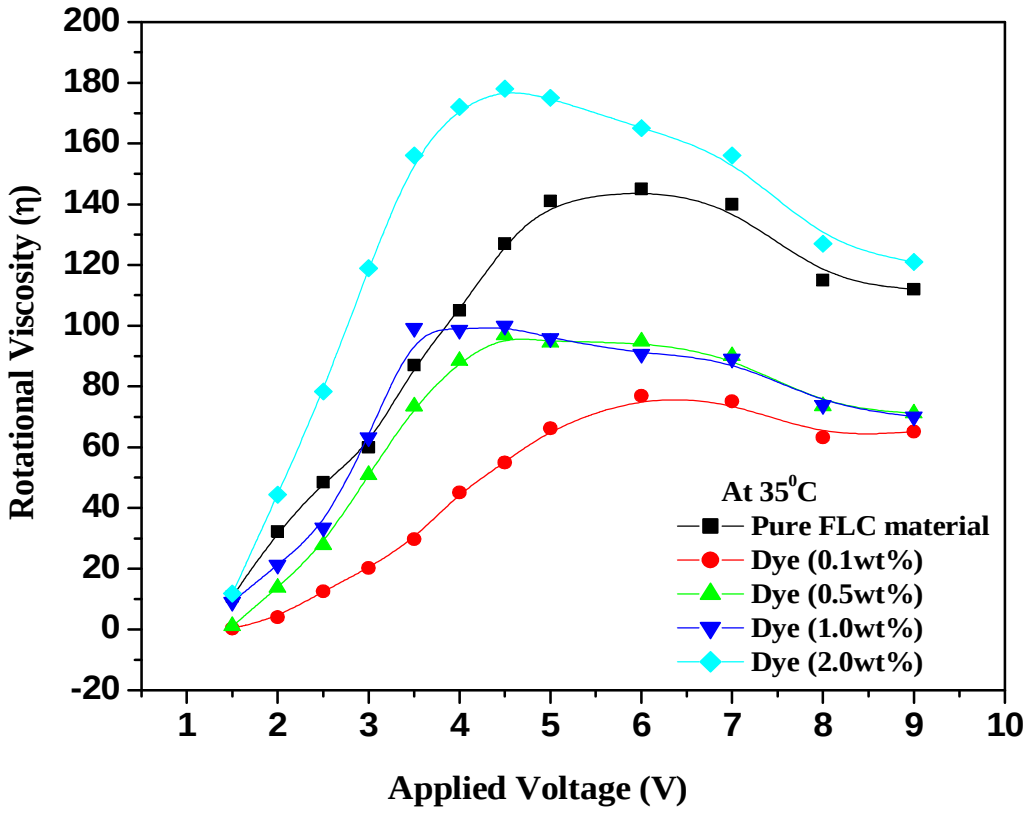


Fig3.13: Variation Of rotational Viscosity with bias voltage

3.2.6: Spontaneous polarization (Ps) of pure and dye dispersed ferroelectric liquid crystal

The variation of spontaneous polarization with bias voltage is shown in Fig3.14. It has been found that the spontaneous polarization at lower dye concentration (0.1, 0.5wt %) increases and then depleted at higher dye concentration. At low concentrations of the dye in FLCs the dye molecules try to fit in the geometry of the system; therefore, dipole moment of dye molecules contributes to the dipole moment of the pure FLC molecules resulting in increase of spontaneous polarization. After certain concentration of dye molecules in pure FLCs matrix, the addition of dye molecules prevents the formation of ferroelectric domains (responsible for existence of spontaneous polarization) and results in the decrease in spontaneous polarization. The optimum concentration point of dye molecules in pure FLCs depends upon the intermolecular interaction of host material and the interaction between the molecules of host and guest molecules.

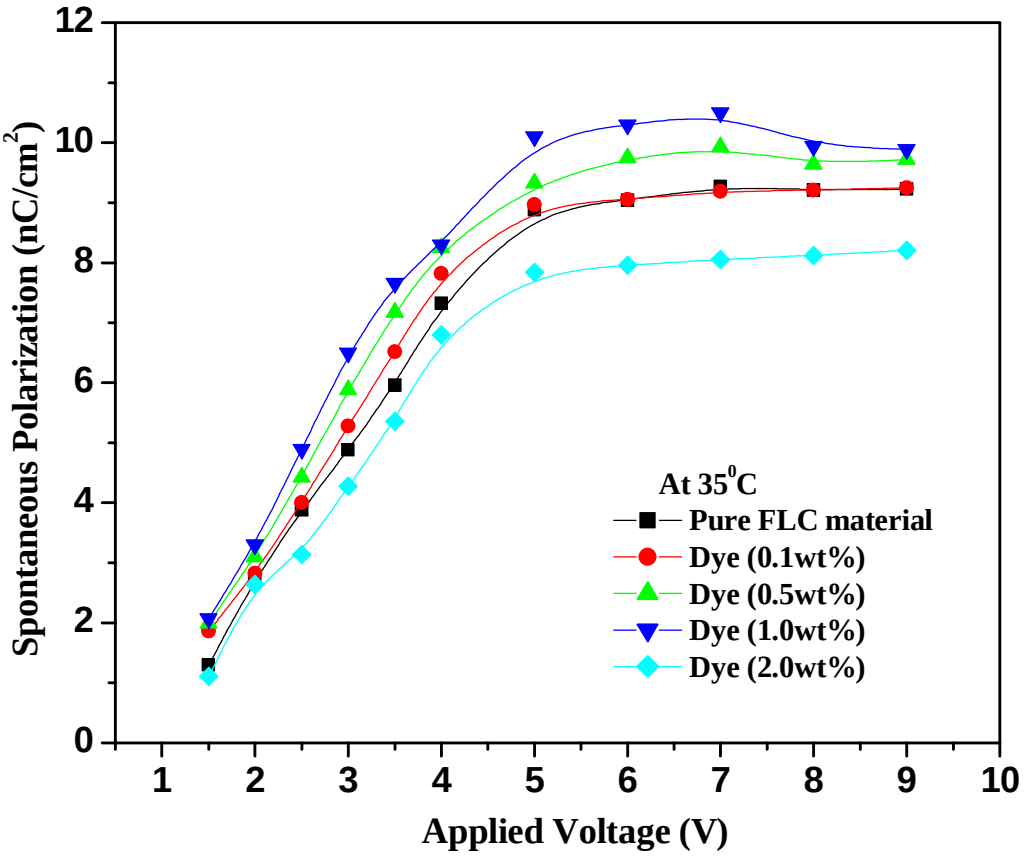


Fig3.14: Variation of spontaneous polarization with bias voltage

Chapter4

Conclusion

In present thesis, the morphological and dielectric properties of pure and dye dispersed FLC mixtures has been investigated. The entire study can be summarized as follows:

1. From morphological investigation we concluded that the texture observed in the reaction mixture were due to the physical interaction of liquid crystal and dye molecules. There is no chemical reaction occur in the compound at any concentration which affect the molecular arrangement.
2. Addition of dye molecule to the ferroelectric liquid crystal material shift the SmC*–SmA phase transition temperature to the lower value. Such phenomena observed in the reaction mixture results the strengthening of helix in SmC* phase due the addition of dye. This strengthening of helix is the combined effect of dipole moment of guest and host molecules, the rotational viscosity and the twist elastic constants of the host.
3. Dielectric behaviour shows strong dependence on the concentration of the dye. As we observed the addition of dye molecule increases the dielectric constant up to 1wt% and at higher concentration it decline.
4. The relaxation frequency of Goldstone mode is higher up to 1wt% dye concentration. However at higher concentration, it depleted to lower side .This type of nature is due to the combined effect of rotational viscosity, elastic constant and helical structure of pure and dye doped FLC mixtures.
5. Effect of bias voltage gives an idea that bias field required to unwind the helix is found to be higher at lower concentration of dye molecule. However at higher concentration, smaller bias field is sufficient enough to unwind the helix.
6. The rotational viscosity of the system increases with the high concentration of dye as dye molecule will obstruct the motion of FLC molecule. But for lower concentrations up to 1wt% rotational viscosity decreases as compared to pure FLC material.
7. Spontaneous polarization of the mixture having less concentration of dye up to 1wt % increases while it decreases as we increase the dye content in the sample as excessive dye prevents the formation of ferroelectric domains.

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