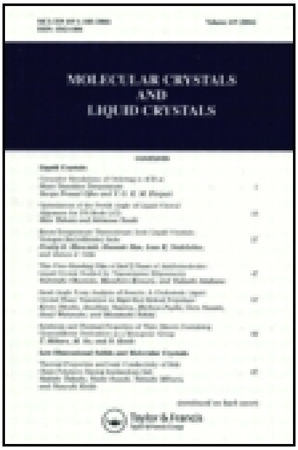

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Dielectric and Electro-Optical Characterization of Dyed Ferroelectric Liquid Crystals

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Dielectric and Electro-Optical Characterization of Dyed Ferroelectric Liquid Crystals

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The ferroelectric liquid crystal displays normally suffers from less contrast ratio and vision angle. To produce high optical contrast and colours in FLC displays, Guest-host mode is widely used. Addition of small amount of dichroic dye in pure FLCs results in considerable change in its dielectric and electro-optical properties. In the present paper we have investigated the effect of two dichroic Anthraquinone dyes (D37 and D5) on the ferroelectric liquid crystal materials (Felix 17/100). Dye doped FLC mixtures have been prepared by the dispersion of each dye at five different concentrations about 1, 2, 3, 4 and 5%wt/wt in pure FLC. The planar aligned cells have been used to study dielectric and electro-optical properties in SmC phase of all pure and the dye doped mixtures. Considerable change in various properties like Goldstone mode relaxation frequency and dielectric strength have been noticed for both the sets of dye doped mixtures. These effects have been discussed in the light of changes produced in the different material parameters like spontaneous polarization, rotational viscosity and tilt angle.*

Keywords: dielectric properties etc.; ferroelectric liquid crystals; guest–host mode

1. INTRODUCTION

In the recent years considerable theoretical and experimental works have been devoted to the study of the dielectric and the electro-optical response of the FLCs due to some serious advantages over the other non-chiral liquid crystals like less response time and spontaneous polarization. Therefore FLCs are getting more attention for

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their use in the display devices, but most of the FLC based displays are black and white and have less contrast. To create an optical contrast in FLC displays primarily two modes are preferred, the birefringence mode and the Guest host mode. The Guest host mode has been investigated in the present study, because this mode provides a high quality display with broad viewing angle, with uniform colours and also avoids the use of polarizers partially or fully. Many researchers have used various types of dye particularly Azo and Anthraquinone dyes in order to improve dichroic ratio of FLC mixtures. The Azo dyes normally have high order parameter and useful in improving the contrast ratio of the Guest host mixture, but these dyes are highly photodegradable [1–4]. The Anthraquinone dyes show high resistance against chemical and photo degradation. Therefore Anthraquinone dyes are preferred for the Guest host mode applications.

Addition of dichroic dye molecule into the pure FLC matrix, results in redistribution of intermolecular energies, hence all of its physical properties particularly the dynamical properties changes drastically. Broad band dielectric spectroscopy is one important tool to understand the dynamical behaviour of such molecular systems.

Therefore the motivation of the present investigation is, to observe the influence of dichroic dye on dielectric and electro-optical behavior of FLC systems. In the present study we report the effect of mixing two different anthraquinone dyes D5 and D37 on dielectric and electro-optical behaviour of a FLC material. For this purpose we have prepared the dye doped mixtures at five different concentrations (1, 2, 3, 4 and 5%wt/wt.).

For better understanding of molecular dynamics due to the coupling of spontaneous polarization and electric field, we have also measured the spontaneous polarization and rotational viscosity for all the samples by using polarising reversal current method [5,6]. One unique quality of this polarization in FLC system is that it is quite sensitive against the change in the environment of the FLC matrix like dye doping. The small change in the FLC matrix may stimulate a large variation in the molecular dynamics. These factors might be of great help for understanding the effects on dynamical behaviour of such pure and dyed FLCs.

Therefore present investigation is supposed to give relevant information about the dye molecules interaction with pure FLC molecule, and how this small perturbation in the FLC matrix affects the different dielectric and electro-optical properties of the pure FLC system. Also how these changes in different properties depends upon the molecular structure of the dichroic dye molecules.

TABLE 1 Basic Parameters of the Ferroelectric Liquid Crystal Felix 17/100

Property	Temp (°c)	Values
Spontaneous polarization	25	47 nC/cm^2
Rotational Viscosity	25	116 mPas
Cone angle (2θ)	25	55.1°
Helical pitch in N*	85	18 µm
Optical anisotropy	30	0.172

2. EXPERIMENTAL DETAILS

Material

The investigated FLC material used in present study is Felix 17/100 (Clariant Chemicals Co. Ltd) and the phase sequence of the sample is Cr – SmC* – SmA – N* – Iso at −20°C, 72°C, 82°C and 95°C. The basic parameters of this FLC material are given in Table 1. The dye doped samples of Felix 17-100 was prepared by dispersion of Anthraquinone dyes D5 and D37 at a five concentrations of 1 to 5%wt/wt ratio in the FLC sample. The mixtures of D5 dye doped Felix 17/100 has been termed as set 1, while the mixtures of pure FLC with second dye i.e., D37 will be termed as set 2 in the paper. Different concentration of each set i.e., 1, 2, 3, 4 and 5% has been termed as mixtures 1, 2, 3, 4 and 5 respectively.

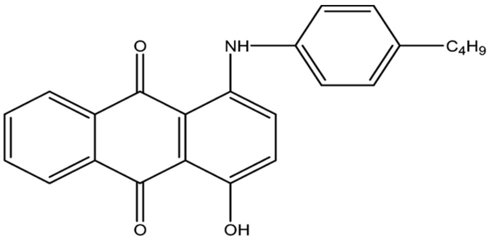
The molecular structure of Anthraquinone dye (D5 and D37) used in this investigation is shown in Figure 1. Heating the mixture up to the isotropic transition temperature of pure FLC and agitating the vial containing Guest host mixture ensured the uniform distribution of dye molecules in the FLC matrix.

Dielectric Permittivity Study

To study dielectric response of mixtures, the capacitance (C_m) and conductance (G_m) of the cell filled with and without material have been determined in the frequency range of 100 Hz to 10 MHz using a computer controlled impedance/gain-phase analyzer (HP-4194 A). Measurement in the high frequency range has been limited to 10 MHz MHz because of the dominating effect of finite resistance of ITO coating on glass plates and lead inductance [7–9].

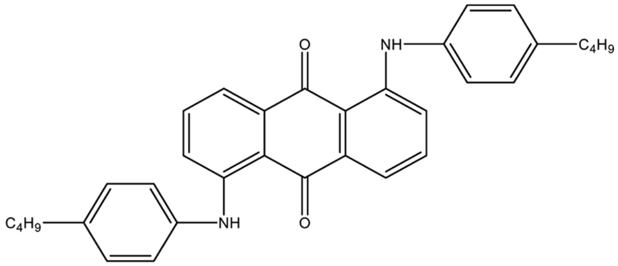
The Cole – Cole equation has been used to analyze the relaxation phenomenon of the pure and dyed FLC such as

$$\varepsilon^* = \varepsilon'(\infty) + \frac{\delta\varepsilon'_{GM}}{1+(i2\pi f\tau_{GM})^{1-\alpha_{GM}}} \tag{1}$$



1-(4-Butyl-phenylamino)-4-hydroxy-anthraquinone

(a)



1,5-Bis-(4-butyl-phenylamino)-anthraquinone

(b)

FIGURE 1 Molecular structure of dye used (a) D5 and (b) D37.

where $\delta\varepsilon'_{GM}$ is the dielectric strength for the Goldstone mode and $\varepsilon'(\infty)$ is high frequency limit of the dielectric permittivity, f is frequency and τ is the relaxation time. The liquid crystals are improper dielectric therefore the dielectric data suffer through the ionic conductivity and electrode polarization problem in low frequency region. In high frequency region data has to be corrected because of finite ITO sheet resistance and lead inductance problem. Therefore measured experimental dielectric data need correction for low and high frequency values. On separating real and imaginary parts of the above equation and after adding high and low frequency correction parameters one may get

$$\varepsilon' = \varepsilon'(dc)f^{-n} + \varepsilon'(\infty) + \frac{\delta\varepsilon'_{GM}[1 + (2\pi f\tau_{GM})^{(1-\alpha_{GM})}\sin(\alpha_{GM}\pi/2)]}{1 + (2\pi f\tau_{GM})^{2(1-\alpha_{GM})} + 2(2\pi f\tau_{GM})^{(1-\alpha_{GM})}\sin(\alpha_{GM}\pi/2)} \tag{2}$$

and

$$\varepsilon'' = \frac{\sigma(dc)}{\varepsilon_0 2\pi f^k} + \frac{\delta\varepsilon'_{GM}(2\tau_{GM})^{(1-\alpha_{GM})}\cos(\alpha_{GM}\pi/2)}{1 + (2\pi f\tau_{GM})^{2(1-\alpha_{GM})} + 2(2\pi f\tau_{GM})^{(1-\alpha_{GM})}\sin(\alpha_{GM}\pi/2)} + Af^m \tag{3}$$

Here $\sigma(dc)$ is the dc ionic conductance, ε_o is free space permittivity and f is the frequency while n, m and k are the fitting parameters. The terms $\varepsilon^{i}(dc)f^{-n}$ and $\sigma(\mathrm{dc})/\varepsilon_o 2\pi f^{k}$ are added in (2) and (3) for correcting the low frequency effect due to the electrode polarization capacitance and ionic conductance [9]. The Af^{m} term is added in (3) for correcting the high frequency effect due to the ITO resistance and lead inductance [10,11]. The other notations are same as given for (1). The experimental data have been fitted in these equations and it has been corrected for low and high frequency values [12].

Electro-Optical Measurement

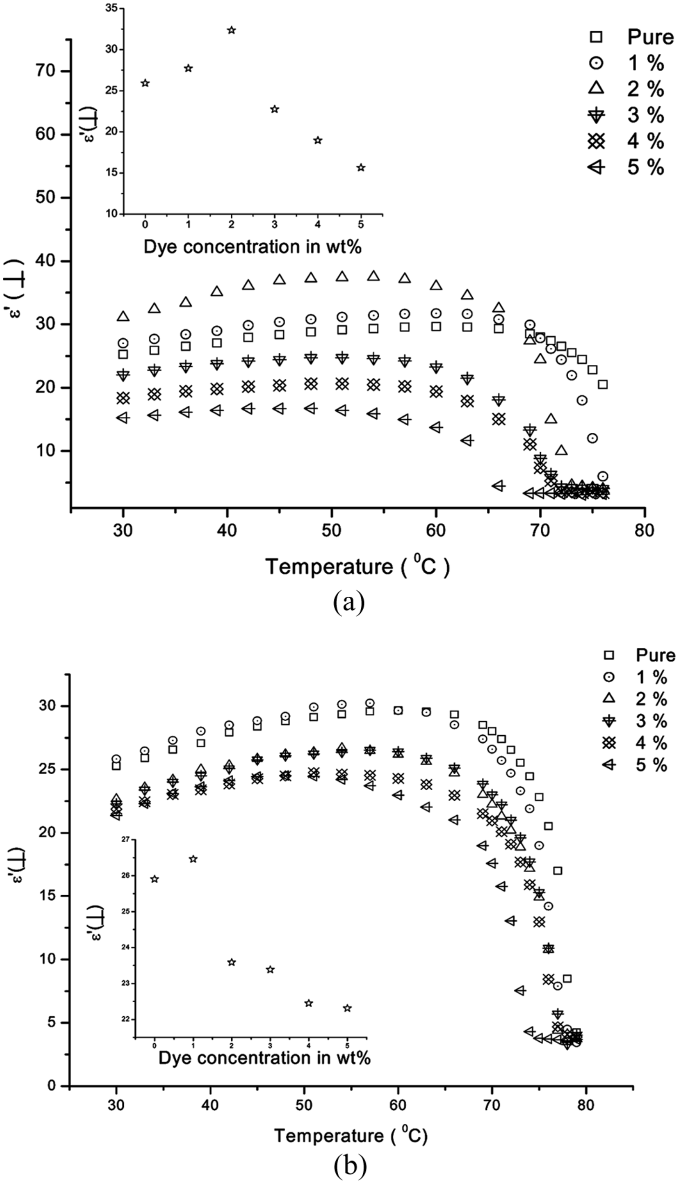
To measure the rotational viscosity and spontaneous polarization of all the samples, polarization reversal current method has been used [7–9]. The complete experimental arrangement for these measurements is well known and has been discussed some where else [9].

Temperature Control

The dielectric constant measurements as a function of temperature have been carried out by keeping the sample on a computer controlled hot stage (Instec HCS-302). Experiments have been performed by ramping the temperature at a very slow heating rate (0.5°C/min). After reaching the required temperature the sample holder has been left for 15 minutes on the same temperature before taking the measurement, so that the thermal equilibrium can be maintained between hot plate and the sample. The whole cycle takes nearly 16 hours and the temperature stability achieved was better than ±0.01°C.

3. RESULTS AND DISCUSSION

Figures 2a and 2b represent the variation of perpendicular component (as the measurements have been done on planar cell) of relative permittivity with temperature for pure and dye doped samples i.e., sets 1 and 2 respectively. The plot of relative permittivity against temperature shows typical ferroelectric liquid crystalline behaviour. It increases first with temperature and after showing the maximum in its value, which also represents the maximum strength of the helix, it starts decreasing near the SmC* to SmA phase transition temperature. The nature of temperature variation of relative permittivity for the dye doped samples i.e., Figures 2a and 2b are same as temperature dependence of relative permittivity for the pure FLC, but the



(a)

(b)

FIGURE 2 Variation of dielectric constant with temperature at the constant frequency of 300 Hz (a) Felix 17/100 with Dye D5 (b) Felix 17/100 with Dye D37. The insets represent dye concentration dependence of the dielectric constant for both set of samples at temperature of 35°C.

magnitude of the relative permittivity changes slightly. The values of relative permittivity were found to increase for the mixtures having lesser concentration of dye i.e., mixtures 1 and 2 of the set 1. But further increment in the concentration of dye results in decrease of relative permittivity as observed for mixtures 3, 4 and 5. Similar behaviour has also been observed for the set 2 but for this dye the host FLC saturates at lower concentrations i.e., relative permittivity increases for the mixture 1 only and show decreasing trends for the mixtures of higher concentrations. This increment in dielectric permittivity has already been reported by our group [7,13] and it is due to the fact that at low concentrations, the dye molecules tries to fit in the geometry of host molecules as in the case for mixtures 1 and 2 of set 1 and mixture 1 for set 2. The dipole moment of the dye molecules contributes to the dipole moment of host molecules, which results in increase in the relative permittivity of mixtures 1 and 2 of set 1 and mixture 1 of set 2 [1,13,14]. But at higher concentrations of dye in pure FLC, excessive dye hinders the formation of ferroelectric domains and consequently the decrease in the values of the relative permittivity has been observed for the mixtures with higher concentrations of dye [7,13]. This fluctuating behaviour of relative permittivity with the percentage concentration of dye in FLCs is closely related with the relaxation frequency of Goldstone mode (Fig. 4). The relaxation frequency increases at lesser concentrations, whereas it decreases for the higher concentrations of dye in comparison to the relaxation frequency of pure FLCs as discussed in the later part of this article.

This anomalous variation in relative permittivity of dye doped FLCs with concentration of dye suggest that after a certain percentage of dye in FLC this increasing trend of relative permittivity is reversed and dielectric properties can not be enhanced simply by adding dye in FLC as shown in inset of Figure 2. This concentration is dependent on the interaction of dye and FLC molecules and is different for different dye FLC systems. It can be termed as saturation concentration for a particular Guest host systems. In our case it is 2% for set 1 and 1% for set 2. This typical behaviour of different dyes is probably due to the small molecular length of dye used in set 1 i.e., D5. Due to this small molecular length, D5 fits easily in to the geometry of the pure FLC, in comparison to D37.

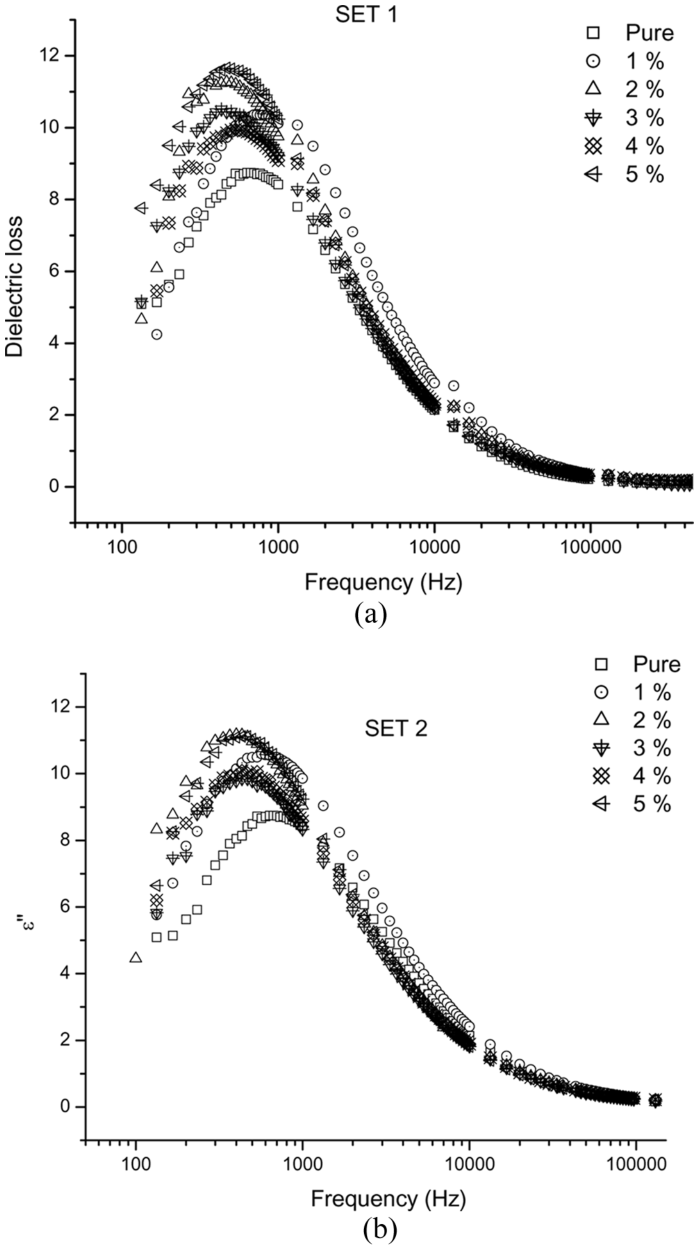
One more important results of these graphs is the shifting of SmC* to SmA phase transition temperature for the dye doped samples as compare to the pure FLC. This phenomenon of shifting of transition temperature has already been discussed in our earlier publications [3].

Figure 3 shows the absorption plot at different temperatures in SmC* phase for pure and dye doped FLCs. The relaxation phenomenon of FLC with a planar alignment is due to the collective dielectric processes such as the Goldstone mode and soft mode [15]. The Goldstone mode dominants over the whole SmC* phase, where as the soft mode appears at higher frequencies near SmC* – SmA phase transition temperature [16]. The relaxation band of the Goldstone mode shifts either towards higher or lower frequency side for the Guest host system in comparison to pure FLC. The mixture having less concentration of dye i.e., before saturation concentration, the relaxation band shift towards high frequency range and for the concentrations above the saturation concentration it shift towards the lower frequency region. This behaviour is also clear from the Figure 4, representing the temperature dependence of the Goldstone mode relaxation frequency. The relaxation frequency for the lesser concentration shifts in higher frequency region, while it shifts towards lower frequency side for the highly doped samples. Such typical behaviour of relaxation frequency can be explained with the help of following equation

$$f_G = \frac{K_3}{2\pi\gamma} q^2 \tag{4}$$

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 rotational viscosity of mixture. It is clear from the Eq. (4) 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.

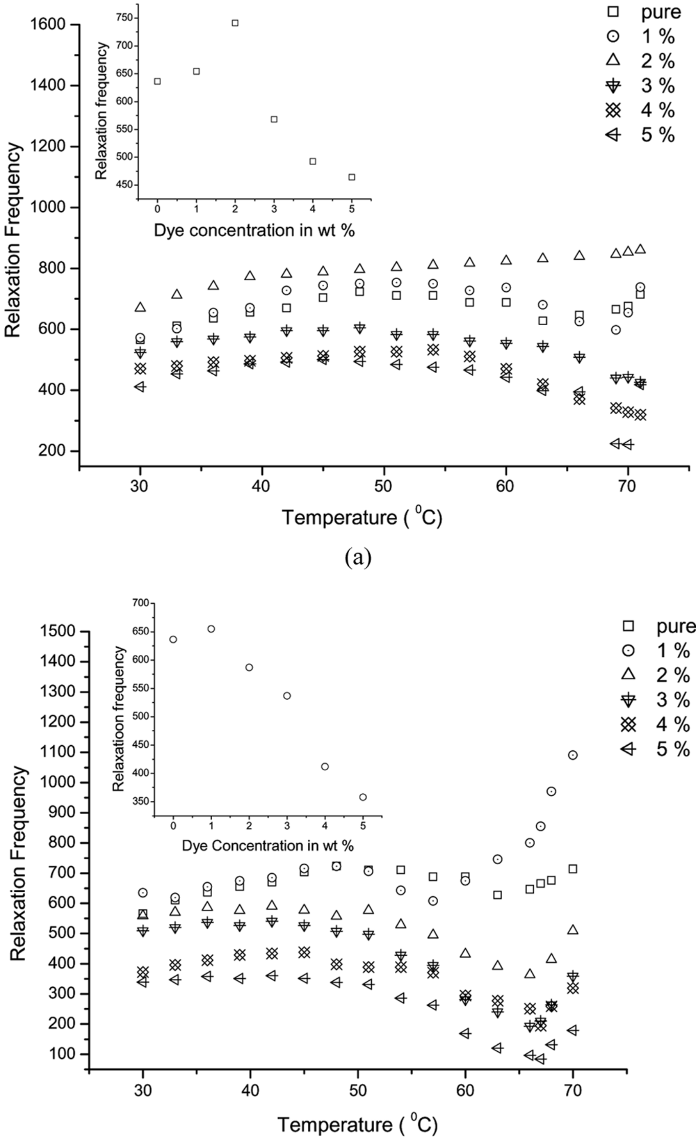
The increase in the relaxation frequency suggests that rotational viscosity for mixture having low concentration of dye than the saturation concentration must be lesser than the rotational viscosity of pure FLC and it should be on higher side for mixtures with the concentration of dye higher than saturation concentration. The lower values of rotational viscosity of Guest host mixture with less concentration of dye do not mean that it is decreased due to addition of dye. But in ferroelectric liquid crystals, the Goldstone mode is basically due to the fluctuation in azimuthal angle. Therefore the effective rotational viscosity in FLC is only due to the Z component of the rotational viscosity [17]. The Z component of the rotational viscosity strongly depends upon the azimuthal angle and this azimuthal angle may alter after the addition of dye in pure ferroelectric liquid crystals matrix. Consequently the rotational viscosity may decrease or increase as observed and presented in Figure 5. For the low concentration of dye, the dipole moment of dye couple with the dipole moment of



(a)

(b)

FIGURE 3 Frequency dependence of the dielectric loss for pure and dye doped Felix 17/100 in SmC* phase at temperature of 35°C (a) for set 1 (b) for set 2.



(a)

(b)

FIGURE 4 Temperature dependence of relaxation frequency for pure Felix 17/100 and its mixture with dye (a) D5 (b) D37. Dye concentration dependence of the relaxation frequency for both set of samples is represented in the respective insets at the temperature of 35°C.

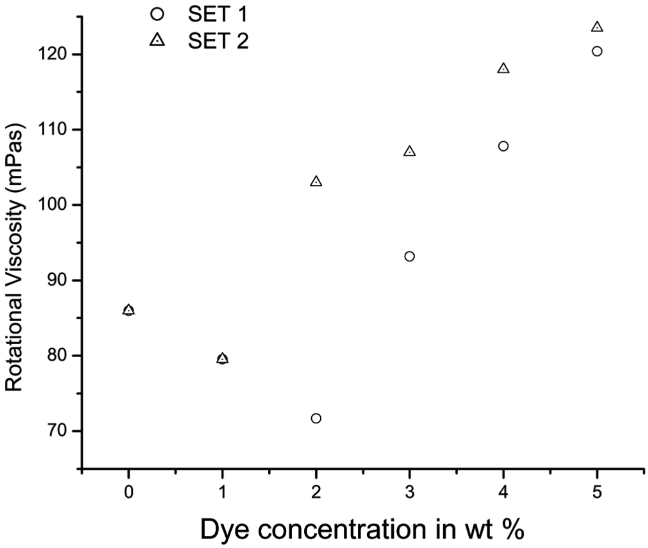
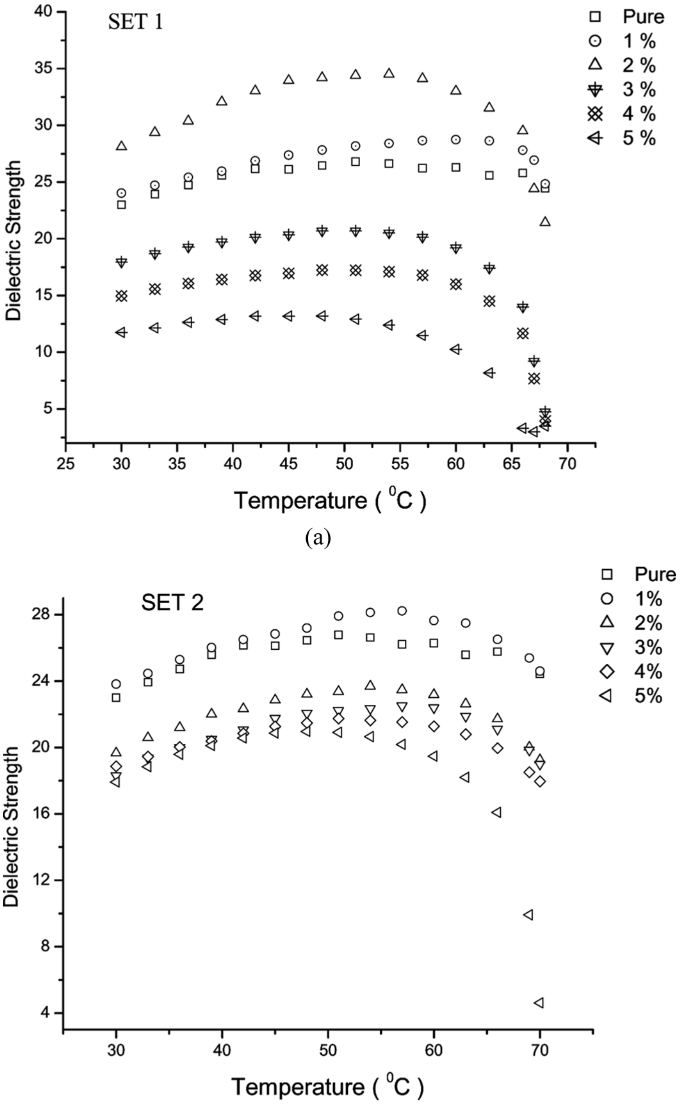


FIGURE 5 Dye concentration dependence of the rotational viscosity for both set of samples.

FLC molecules. While for the highly dye doped mixture (i.e., beyond the saturation concentration), dye molecule will obstruct the motion of FLC molecule as a result of which rotational viscosity increases and causes decrease in relaxation frequency and relative permittivity as well.

The relaxation strength has been evaluated by fitting the Cole-Cole equation into the experimental data as disscussed in experimental section [7]. An appriciable change has also been noticed for the relaxation strength of Goldstone mode for both the sets of samples as shown in Figure 6. Again the similar behaviour i.e., pre and post saturation concentration phenomenon in the value of dielectric strength, has been noticed. The relaxation strength of mixtures 1 and 2 of set 1 and mixture 1 of set 2 increases as compare to the relaxation strength of pure FLC, while for other mixtures of both the sets, it is found to decrease in comparison to the relaxation strength of pure Felix 17/100 in SmC* phase. The variation of relaxation strength with temperature for Goldstone mode is in agreement with theoretical equation in term of spontaneous polarization and tilt angle such that [18–20]:

$$\Delta\varepsilon_{GM} = \frac{P_S^2}{2K_3 q^2 \theta^2} \tag{5}$$



(a)

(b)

FIGURE 6 Temperature dependence of dielectric strength (a) for mixtures of set 1 (b) mixtures of set 2.

Here, P_S is spontaneous polarization, whereas θ represents tilt angle. The dielectric strength directly depends upon the spontaneous polarization. Therefore this type of behaviour of dielectric strength

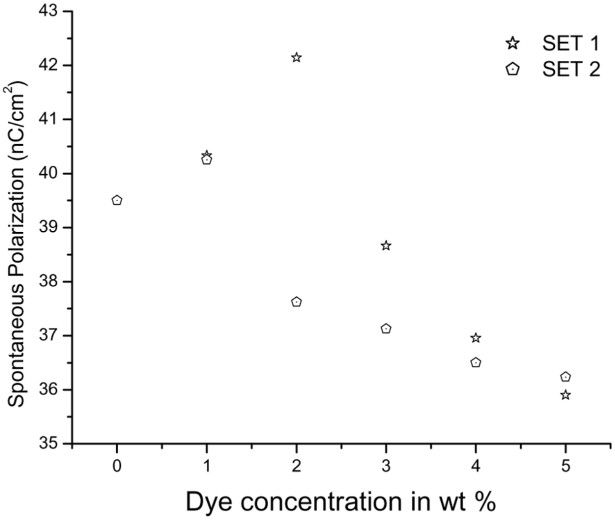
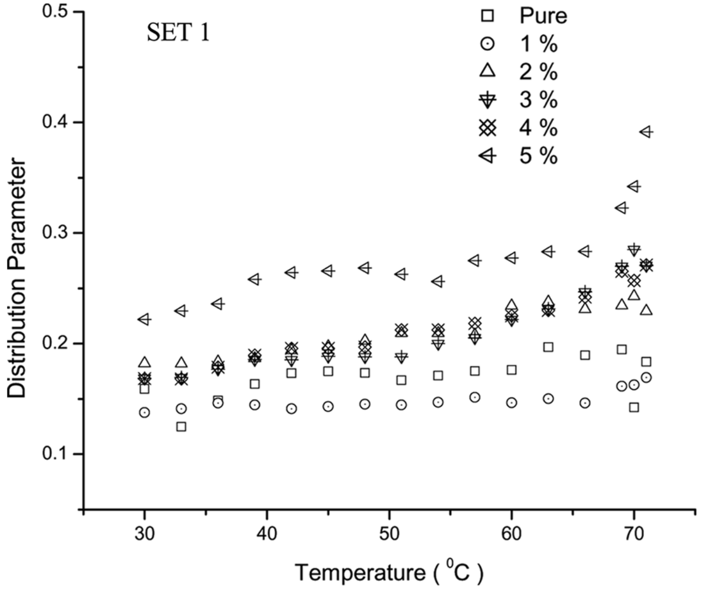


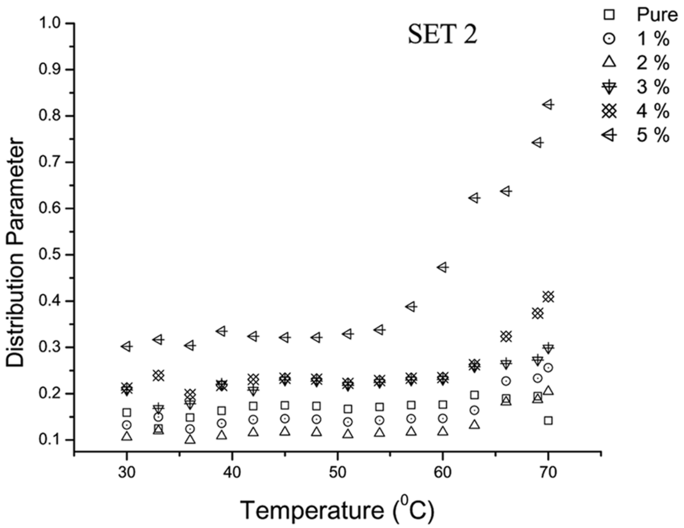
FIGURE 7 Variation of spontaneous polarization with the concentration of dye in pure FLC geometry for both set.

in conjunction with the above equation suggest that the spontaneous polarization of the mixture having less concentration of dye than the saturation concentration, increases, while for mixtures having higher concentration than that saturation concentration, spontaneous polarization should decrease. This spontaneous polarization values have been determined with the help of electro-optical method and it has been found that spontaneous polarization variation is same as predicted above. The variation of spontaneous polarization is shown in Figure 7. The decrease in the value of spontaneous polarization is due to the fact that addition of excessive dichroic dye molecules in pure FLC geometry affects the existing configuration of ferroelectric domain, (responsible for the existence of spontaneous polarization). Thus a decrement in the value of spontaneous polarization has been observed for the highly doped sample (the concentrations above the saturation concentration of dye in pure FLC matrix) of both the sets.

The materials like liquid crystals, materials with long molecular chain and polymers show broader dispersion of relaxation time. Therefore in 1941 Cole and Cole [21] have suggested the existence of distribution parameter, which is also defined as degree of distribution of relaxation time. The temperature dependence of distribution parameter for pure FLC and the dye doped mixtures i.e., set 1 and 2 have been shown in Figure 8. The distribution parameter



(a)



(b)

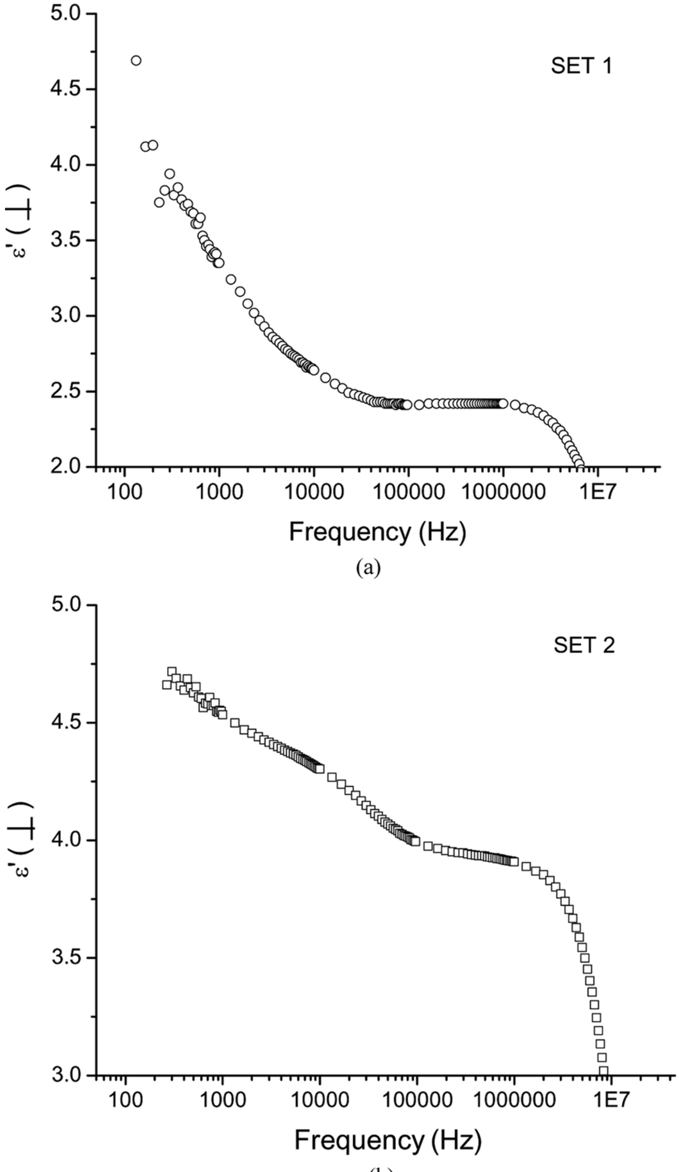
FIGURE 8 Variation of distribution parameter with temperature (a) for set 1 (b) for set 2.

for pure FLC mixture increases at higher temperatures. This smaller values of distribution parameter at lower temperatures of SmC* phase for pure FLC mixture clearly indicates that Goldstone mode predominates over the Soft mode in SmC* phase, while the soft mode comes into existence near the SmC* – SmA phase transition temperature [22] due to which the value of distribution parameter increases in vicinity of SmC* – SmA phase transition temperature. Similar temperature dependence has also been noticed for the dye doped samples but the values of distribution parameter show the opposite dye concentration dependence for both set of samples as compared to the other properties i.e., it shows the decreasing trend for the samples having less concentration and found to increase for the higher concentrations of dye in Guest host mixtures. The values of distribution parameter for the mixture 5 of both set of samples is found to increase more rapidly near the SmC* – SmA phase transition temperature than other mixtures, and this value of distribution parameter is too much higher in comparison to other mixtures. This unusual increase in the value of distribution parameter is the clear indication of presence of more than one relaxation mode in both the set of the samples. To confirm the fact the relative permittivity plot against the frequency has been zoomed and shown in the Figure 9. A clear existence of the some relaxation process near 30 KHz has been confirmed for the mixture 5 of set 2, while for set 1 it is not very much clear. We are unable to show the dispersion peeks for such relaxation process because the values of the dielectric loss for such relaxation are very small and lies under the limits of experimental error.

One may confuse by such plots for the existence of some new relaxation process as a consequence of presence of dye molecules into the FLC geometry, but we should clear it that this relaxation mode is not a new relaxation mode but the soft mode. Usually the soft mode of relaxation phenomenon occurs in high frequency region, but in the present case it is some where near 30 KHz [23,24]. The soft mode of relaxation in SmC* phase is related with fluctuation of amplitude of the tilt and could be defined by following equation:

$$F_S = \left(Kq^2 + \alpha(T - T_C^*)\frac{1}{\gamma}\right)/2. \tag{6}$$

Here F_S represent relaxation frequency in soft mode, α is a constant and γ is the rotational viscosity. While the T_c^* shows the SmC* to SmA phase transition temperature. In our earlier paper we have reported that addition of dichroic dye in to pure FLC



(a)

(b)

FIGURE 9 Variation of relative permittivity with frequency at the temperature of 67°C (a) for the mixture 5 of set 1 (b) mixture 5 of set 2.

geometry offers more hindrance for the amplitude fluctuation i.e., higher rotational viscosity and results in decrease in the relaxation frequency of the pure FLC [2]. This decrease will be maximum for the highly doped FLCs. It has also been reported that the relaxation strength of soft mode increases for the dyed FLCs [5], and will increase at higher concentrations of dye.

In the present study we are not able to observe the soft mode of relaxation for pure FLC. But as the dye concentration is increased in the FLC the relaxation strength increases and the soft mode comes in to existence at the higher concentration of dye i.e., at 5% (mixture 5) of both samples. The presence of soft mode is very much clear for the set 2 i.e., D37 doped samples. Because of the bigger molecular length of the D37 this dye will offer much hindrance for the amplitude fluctuation consequently decreases the relaxation frequency considerably and contribute to the relaxation strength of the soft mode, potentially. But for the Set 1 it is not clear very much as shown in the Figure 9(a). We may get the similar phenomenon at some higher concentration of the dye D5 in the pure FLC.

4. CONCLUSIONS

The whole study can be summarized as follows:

1. The observation of anomalous variation in relative permittivity, relaxation frequency, spontaneous polarization and rotational viscosity at higher concentration of dye in pure FLC, conclude that after a certain percentage of dye in pure FLC, instead of enhancement in various properties, dye doping decreases them all. This concentration is dependent on the interaction between dye and FLC molecules and must be different for different systems. This concentration is termed as saturation concentration for a particular Guest host systems.
2. Addition of dye molecules into pure FLC matrix changes the values of relative permittivity. This change depends upon the concentration of dye in pure FLC, structure of dye molecule and how the dipole moment of dye molecule interacts with the dipole moment of host molecules.
3. The relaxation frequency of Goldstone mode shifts toward higher frequency side for mixtures 1 and 2 of set 1 and for mixture 1 of set 2, while for other mixtures it shifts towards lower frequency side suggesting that Goldstone mode for sample with high concentration of dye (concentration larger than the saturation

concentration) become slower than the other mixtures and pure FLC. This type of nature is due to the combined effect of rotational viscosity, and helical structure of pure and dye doped FLC mixtures.

4. Relative permittivity plot against the frequency clearly shows the presence of new relaxation phenomenon, but in fact it is the soft mode whose relaxation frequency is decreased due to the addition of dye molecules in to the pure FLC matrix.

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