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## Effects of dichroic dye on the dielectric properties of ferroelectric liquid crystal mixture

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**Abstract.** The dielectric spectroscopy of the ferroelectric liquid crystal mixture FLC-6980 doped with a low concentration (~2% wt/wt) of anthraquinone dye has been studied. The complex permittivity has been measured in the frequency range 100 Hz to 1 MHz in  $SmC^*$  and  $SmA$  phases. Dielectric increments and the relaxation frequencies at various temperatures have been evaluated. Our results indicate that the relaxation frequency and the  $SmC^*$ – $SmA$  transition temperature  $T_{C^*A}$  decreases whereas the dielectric increment increases about 2.5-fold on dye addition.

### 1. Introduction

Extensive studies have been carried out to understand the dielectric spectroscopy of ferroelectric liquid crystals (FLCs) and their mixtures [1–11]. It gives information about the collective and non-collective excitations of the molecules. The dielectric response mainly consists of two modes below 1 MHz in the  $SmC^*$  phase. These modes are related to the director fluctuations known as the Goldstone mode (GM) and the soft mode (SM). The GM appears due to the fluctuations in the azimuthal orientation of the director in the  $SmC^*$  phase. The SM is due to the fluctuations in the amplitude of the tilt angle and appears in the vicinity of the  $SmC^*$ – $SmA$  ( $T_{C^*A}$ ) transition temperature. The complex permittivity of the  $SmC^*$  phase is dominated by the GM [12, 13]; however it can be suppressed by application of a bias field resulting in the unwinding of the helicoidal structure. Recently, Beresnev *et al* [14] and Wrobel *et al* [15] have reported the observation of new relaxation processes in ferroelectric liquid crystal with high spontaneous polarization after the suppression of the GM under the influence of bias voltage.

The director reorientation can be described in terms of the real [ $\epsilon'(\omega, T)$ ] and imaginary [ $\epsilon''(\omega, T)$ ] part of the complex dielectric permittivity [ $\epsilon^*(\omega, T)$ ] which is given as:

$$\epsilon^*(\omega, T) = \epsilon'(\omega, T) - i\epsilon''(\omega, T) \quad (1)$$

where  $\omega = 2\pi f$  is the angular frequency of the applied electric field and  $T$  is the temperature.  $f$  is the characteristic frequency connected to relaxation mechanisms which contribute to  $\epsilon^*(\omega, T)$  and is given by [12]:

$$\epsilon^*(\omega, T) = \epsilon_\infty(T) + \sum_{j=1}^4 \frac{\delta\epsilon^j(T)}{1 + (i\omega\tau_j)^{1-\alpha_j}} \quad (2)$$

where  $\delta\epsilon^j = \epsilon_0^j - \epsilon_\infty^j$  are the respective dielectric increments which is the difference between the values of  $\epsilon'(\omega, T)$  at low and high frequencies respectively for (1) the GM, (2) the new

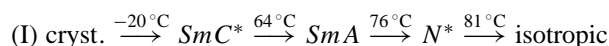
relaxation mode (NRM), (3) the SM and (4) the molecular mode (MM).  $\epsilon_\infty$  is the high frequency limit of the electric permittivity.  $\tau_j$  and  $\alpha_j$  are relaxation times and distribution parameters respectively for the  $j$ th mode. (Hereafter,  $\epsilon'(\omega, T)$  and  $\epsilon''(\omega, T)$  will be written as  $\epsilon'$  and  $\epsilon''$  respectively.)

A review of the literature reveals that the effects of dichroic dyes in liquid crystals have been investigated extensively for their use in electro-optic display devices [16–18]. However, no serious effort has gone into the understanding of the dielectric properties of FLCs containing dye molecules although dielectric relaxation in such systems has been reported recently [11]. It has, therefore, been considered worthwhile to make a systematic and detailed dielectric study of a ferroelectric liquid crystal mixture containing a low concentration of anthraquinone (AQ) dye in planar cells. These investigations are expected to give information about the interaction of dye molecules with liquid crystals and its contribution to the occurrence of relaxation modes.

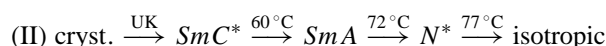
## 2. Experiment: Sample preparation

We have used a multi-component ferroelectric liquid crystal mixture FLC-6980 [19] as a host material. It has a long helical pitch ( $\sim 12$ – $15 \mu\text{m}$ ), low spontaneous polarization and tilt angle  $\sim 25^\circ$ . The dye doped sample of FLC-6980 was prepared by the dispersion of a low concentration of  $\sim 2\%$  wt/wt ratio AQ dye in the liquid crystal mixture. The molecular structure of the AQ dye used in the study is shown in figure 1 [20]. The uniform distribution of the dye molecules in the liquid crystal matrix was ensured by heating the mixture to the isotropic temperature of the liquid crystal and then agitating the vial containing the mixture. We call this sample the guest–host mixture (G–HM). Two LUCID cells [21] of  $7.5 \mu\text{m}$  thickness each were filled with FLC mixture (FM) and G–HM respectively by capillary action. These cells essentially consist of indium tin oxide (ITO) coated glass substrates pretreated with polyimide. This gives planar alignment to the sample as was confirmed by the thermal polarizing microscopy at an accuracy of  $0.1^\circ\text{C}$  using a Mettler temperature programmer cum hot stage (model TP 5 and TP52). The strong interaction between the two different types of molecule also encourages the sample to maintain good alignment [22].

The phase sequence of two mixtures as observed by optical textures is given by: FLC mixture (FM) [19]



and guest–host mixture (G–HM)



(UK is unknown value). We note that the addition of dye decreased the transition temperatures  $T_{C^*A}$  and  $T_{AN^*}$  of the sample by about  $4^\circ\text{C}$ . The sample cell was connected to a Hewlett–Packard impedance analyser model HP 4192A to obtain the values of capacitance and dissipation factor ( $D$ ). The cells were first calibrated using air and benzene as standard references.

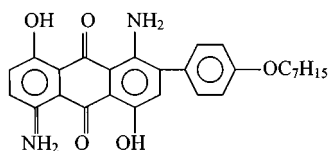


Figure 1. Molecular structure of anthraquinone dye used.

### 3. Results and discussion

The typical variation of  $\epsilon'$  as a function of reduced temperature ( $\Delta T = T - T_{C^*A}$ ) for FM and G-HM is shown in figure 2. It is seen that below 1 kHz there is a marginal increase in the value of  $\epsilon'$  with increasing temperature for both the samples. A comparison of the data reveals that the permittivity in case of G-HM is higher by approximately 2.5 times than that of the FM. This increase can be explained as due to the corresponding increase in spontaneous polarization ( $P_S$ ) of FM with addition of dye molecules as reflected in figure 3. Here, the solid line corresponds to the mean square root fit law given by

$$P_S = A(T_{C^*A} - T)^\alpha \tag{3}$$

where  $P_S$  is the magnitude of the spontaneous polarization at a given temperature,  $A$  is the material constant and the exponent  $\alpha = 0.5$ . The  $\alpha$  factor obtained from the mean square fit is in agreement with the mean field theory. We notice that  $P_S$  increases in the same manner as the dielectric permittivity. As each dye molecule has preferential direction of orientation, it is expected to become aligned along the host molecules. Thus freedom of movement of

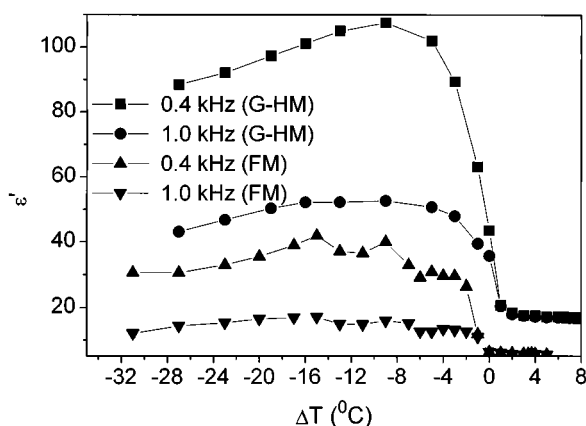


Figure 2. Temperature dependence of  $\epsilon'$  for G-HM and FM at 0.4 kHz and 1 kHz.

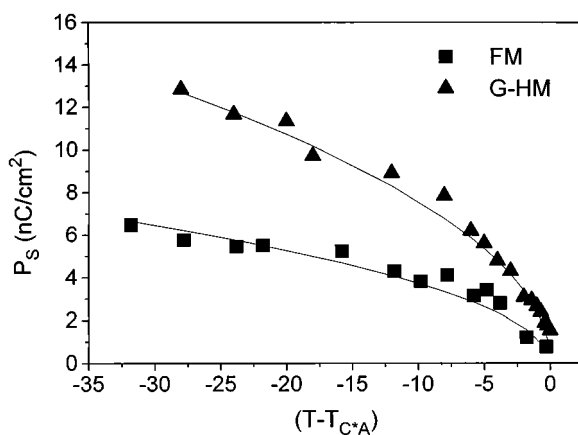
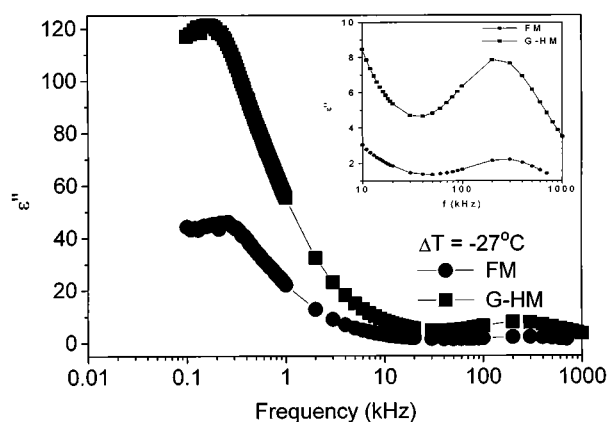
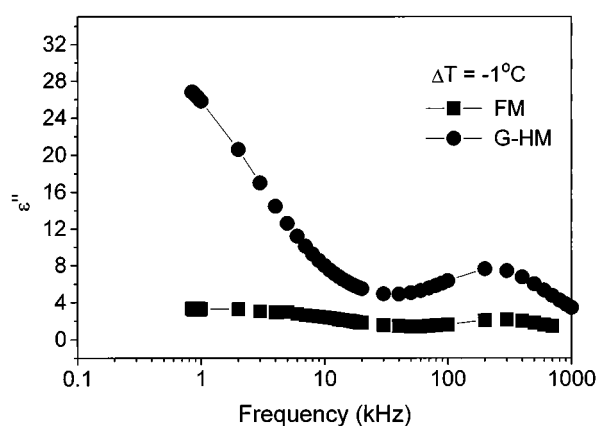


Figure 3. Temperature dependence of spontaneous polarization for (a) G-HM and (b) FM.



(a)



(b)

**Figure 4.** Frequency dependence of  $\epsilon''$  (a) at  $\Delta T = -27^\circ\text{C}$  and (b)  $\Delta T = -1^\circ\text{C}$  for G-HM and FM.

the molecules is hindered and the dipole moment of the dye molecules contributes to the host molecules.

The frequency dependence of  $\epsilon''$  in the  $SmC^*$  phase at  $\Delta T = -27^\circ\text{C}$  is shown in figure 4(a) for FM and the G-HM. It is seen that beyond 100 kHz,  $\epsilon''$  increases and attains a maximum at 232 kHz. We believe that it is a representation of a new relaxation process denoted by NRM. As shown in figure 4(a) inset, the relaxation is dominant in the case of the dyed sample by an order of magnitude. This increase can be explained on the basis of the fact that surface stabilized and the higher spontaneous polarization states in the G-H mixture will give rise to strong surface anchoring effects in the thin cells. The formation of tiny ferroelectric domains in these cells and their contribution to  $\epsilon''$  will eventually contribute to the appearance of this mode. The dielectric response in the  $SmC^*$  phase comes from the GM having relaxation frequency in the range of 0.15–0.3 kHz. It is clear that there are dispersion effects in the  $SmC^*$  phase due to the GM at low frequencies and NRM at higher frequencies (away from the  $T_{C^*A}$  in the  $SmC^*$  phase). Similarly as we approach the transition temperature  $T_{C^*A}$ , the SM starts appearing (shown in figure 4(b)).

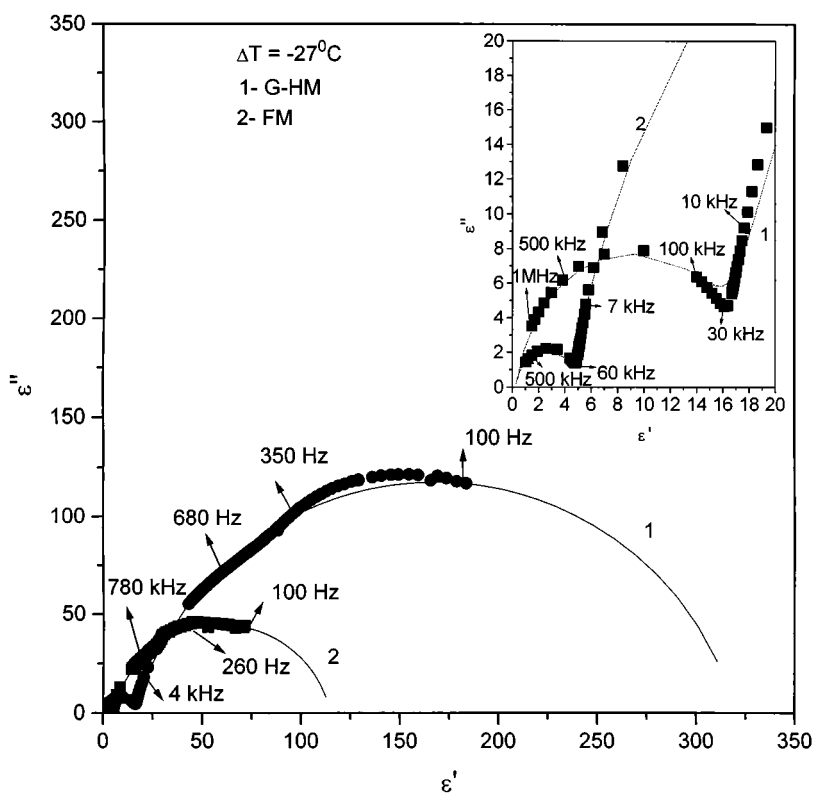


Figure 5. Cole-Cole plot for the GM and NRM at  $\Delta T = -27^\circ\text{C}$  of the G-HM and FM.

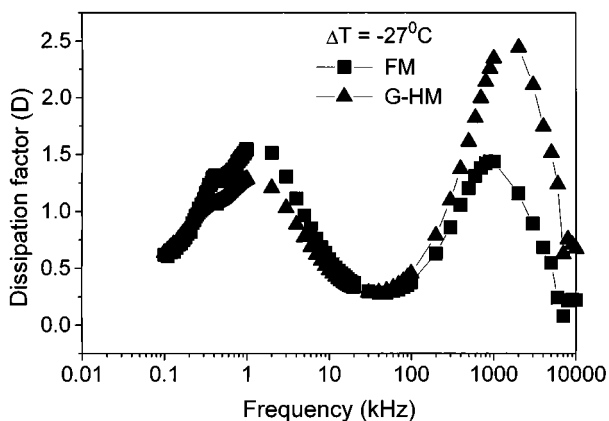
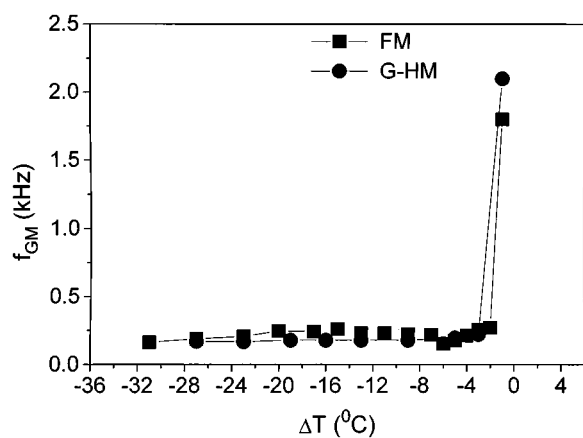
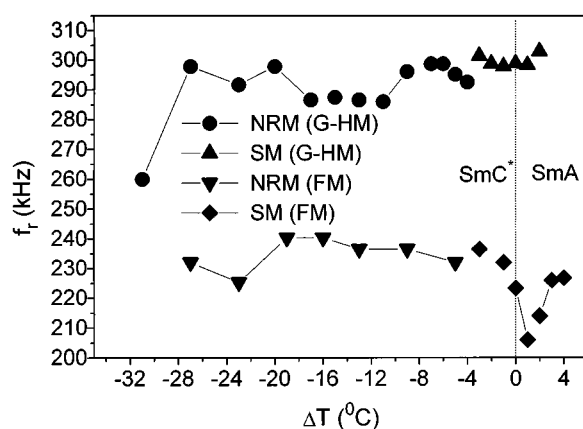


Figure 6. Frequency dependence of the dissipation factor ( $D$ ) at  $\Delta T = -27^\circ\text{C}$ .

The Cole-Cole plot corresponding to the relaxation phenomena for the FM and G-HM at  $\Delta T = -27^\circ\text{C}$  is shown in figure 5. In both cases, the plot indicates two relaxation processes corresponding to two semi-circles. The solid lines in the plot correspond to the theoretical curves by fitting the experimental data in equation (2). The permittivity values reflect the occurrence of the relaxation modes which is dominant in the G-HM.



(a)



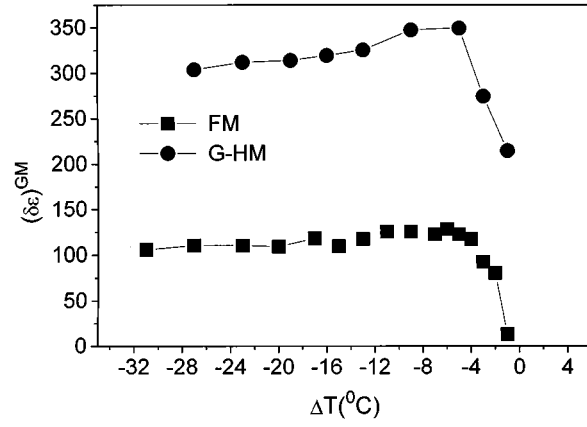
(b)

**Figure 7.** Relaxation frequency versus reduced temperature of (a) GM and (b) SM and NRM for G-HM and FM.

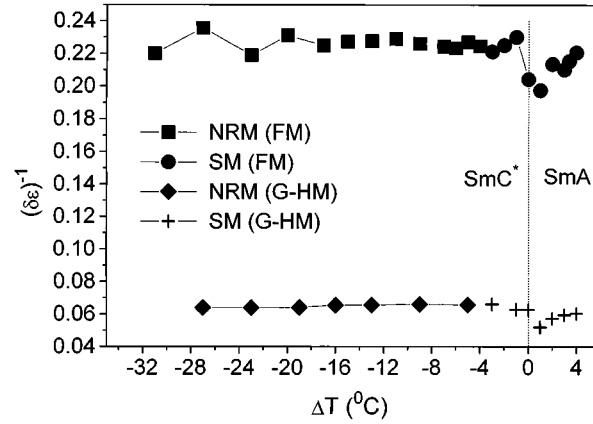
The dissipation factor ( $D$ ) as a function of frequency at  $\Delta T = -27^\circ\text{C}$  is shown in figure 6. It is seen that  $D$  behaves differently below 30 kHz than above this frequency. The opposite effects might be due to the different size of molecular constituents of the dye and liquid crystal in the G-HM which shows dominant effects at high frequencies.

We notice that there is a significant variation in dielectric parameters on addition of the dye to the FM as shown in figures 7 and 8. As seen, the  $f_{GM}$  does not change significantly at room temperature on dye addition (figure 7(a)); however significant variations are noticed in the relaxation frequencies of the NRM and SM shown in figure 7(b). Our results corresponding to figures 7(a) and 8(a) indicate that  $f_{GM}$  and  $\delta\epsilon^{GM}$  are almost independent of temperature away from the transition but vary sharply near the transition. This variation shows the suppression of the GM at this temperature. The variation of the  $\delta\epsilon^{GM}$  with temperature for the FM and G-HM in terms of polarization ( $P$ ) and tilt angle ( $\theta$ ) is governed by the equation

$$\delta\epsilon^{GM} = \frac{P^2}{2\epsilon_0 K_\phi q^2 \theta^2} \quad (4)$$



(a)



(b)

**Figure 8.** Temperature dependence of (a) dielectric increment  $(\delta\epsilon)$  of GM and (b)  $(\delta\epsilon)^{-1}$  of SM and NRM in G-HM and FM.

where  $K_\phi$  is the elastic constant,  $q$  is the wavevector and  $\epsilon_0$  is the dielectric permittivity in free space. The temperature dependence of  $f_{GM}$  very well fits with theory for higher values of the dimensionless parameter ( $\beta$ ) which is given as

$$\beta = \frac{\tilde{C}\tilde{\epsilon}\eta^{1/2}}{\Omega^{1/2}} \quad (5)$$

where  $\tilde{C}$ ,  $\tilde{\epsilon}$ ,  $\Omega$  and  $\eta$  are renormalized constants. In the vicinity of the transition temperature, SM dielectric parameters [ $f_{SM}$ ,  $(\delta\epsilon^{SM})^{-1}$ ] have been shown to vary linearly with temperature according to the relation [23, 24]:

$$f_{SM} = a(T - T_C) + b \quad (6)$$

where  $a$  and  $b$  are constants.

The relaxation frequency and inverse of dielectric increment for the NRM and SM are shown in figure 7(b) and figure 8(b) respectively. The slope of the  $(\delta\epsilon^{SM})^{-1}$  and  $f_{SM}$  versus reduced temperature have been evaluated in the  $SmC^*$  phase as well as in the  $SmA$  phase for



the FM and G–HM. The ratios of the slopes in  $SmC^*$  and  $SmA$  for  $(\delta\epsilon^{SM})^{-1}$  and  $f_{SM}$  for the FM sample are  $-2.5$ ,  $-1.5$  and for G–HM doped they are  $-1.1$ ,  $-0.41$  respectively. The values of these parameters reported in the literature for many pure substances [25] and for mixtures [26] near the transition have been found between  $-0.2$  and  $-4.0$ . These variations in the dielectric parameters in the FM and G–HM may be due to the change of order parameter and viscosity with dye addition.

#### 4. Conclusions

(1) We have investigated the dielectric spectroscopy of an FLC mixture to understand the effects of the dichroic dye in it. It has been found that the dielectric spectrum consist of GM, NRM in the  $SmC^*$  phase and SM in the vicinity of  $T_{C^*A}$ .

(2) A new relaxation mode has been observed in both the cases. The relaxation frequency of this mode is lower for the G–HM as compared to FM. This mode might have resulted due to the formation of tiny ferroelectric domains and strong surface anchoring effects.

(3) The permittivity of dye doped mixture is 2.5-fold greater than the FM. This indicates that the dye molecules contribute to the increase in spontaneous polarization and the permittivity.

(4) Spontaneous polarization in the  $SmC^*$  phase follows the mean square root law for both the G–HM and FM.

(5) The relaxation frequency and  $T_{C^*A}$  transition decreases while the dielectric increment increases on the addition of dye. Relaxation frequency and dielectric increment for the GM and NRM are independent of temperature while near  $T_{C^*A}$  these parameters vary sharply for the GM. The decrease in the relaxation frequency means that the flexibility of the molecules in the G–HM is lower as compared to that in the FM.

(6) The SM dielectric parameters in the near vicinity of  $T_{C^*A}$  vary linearly with temperature. The slope ratios for relaxation frequency and inverse of dielectric increment for FM are  $-2.5$ ,  $-1.5$  and for G–HM they are  $-1.1$ ,  $-0.41$  respectively.

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