Molecular Crystals and Liquid Crystals

Dielectric and Electrical Investigations in Pure and Dyed Short Pitch High Spontaneous Polarization Liquid Crystals

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First published on: 08 July 2010

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The dielectric and electrical properties of a short pitch and high spontaneous polarization ferroelectric liquid crystal mixture and its guest–host derivatives with different wt/wt ratio of anthraquinone blue dichroic dye are studied. The increase in dye concentration results in the decrease of the permittivity as well as polarization of the material in the SmC* phase. However, an opposite effect is observed in permittivity, in the SmA* phase, and in polarization near the T_C. The response time of pure material is found to be less than the dyed samples with no appreciable change in viscosity.

Keywords Anthraquinone dye; dielectric strength; ferroelectric liquid crystals; guest-host mixtures; relaxation frequency

Introduction

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-decycloxy benzylidine p-amino-2-methylbutyl cinnamate (DOBAMBC) exhibiting chiral smectic C (SmC*) phase [1]. Ferroelectric liquid crystals (FLCs) are ideally suitable for the electrooptic devices because of their inherent tendency to form oriented, optically birefringent domains and can be utilized in many ways for light modulation purposes [2]. They can act as light-scattering centers or can rotate the plane of polarization of light. A considerable experimental and theoretical study has been carried out to understand the various dielectric and electrical properties of these materials [3–9].

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Electrical studies help in measuring polarization, response time, viscosity, *etc.*, whereas dielectric investigations reveal information regarding the molecular and relaxation processes of various phases of ferroelectric liquid crystals. The SmC* phase, possessing helicoidal structure (Fig. 1), has four relaxation modes; two are the high-frequency polarization modes and the other two are low-frequency director relaxation modes, as confirmed by the dielectric studies. The low-frequency modes are called the *Goldstone mode* (GM) and the *soft mode* (SM). The GM is due to the fluctuation in the phase of an azimuthal angle (angle representing tilt direction) and SM is due to the fluctuation in the amplitude of the tilt angle (angle between layer normal z and director **n**). Far from the transition to SmA*, only GM contribute toward permittivity in SmC* phase, whereas in the vicinity of T_C (SmC*-SmA* transition temperature) both modes contribute to dielectric spectrum. In the SmA* phase, however, the contribution to permittivity is only from soft mode. Recently, some more relaxation modes, namely, bulk domain mode (BDM) and new relaxation mode (NRM), have also been reported in ferroelectric liquid crystal mixtures in the SmC* phase [10–16]. These modes appear in the presence of an external electric field [16]. The BDM appears due to the interaction of bulk domains with electric field, whereas NRM arises due to the coupling of surface domains with field.

Ferroelectric liquid crystals, when doped with small quantities of anthraquinone dye, exhibit interesting behavior. Raina *et al.* [12] showed that the FLCs doped with dichroic dyes have a strong influence on the parameters of their dielectric modes. They studied an FLC mixture having long helix pitch but low spontaneous polarization (P_s). The structure of the material was surface-stabilized ferroelectric (SSF) liquid crystal. Their results indicated that the complex permittivity and polarization increases in the dye-doped samples as the relative coupling with dye molecules influences the order parameter and increases dipolar interactions at the molecular level.

In the present study, an attempt has been made to investigate such behavior in a novel ferroelectric liquid-crystal mixture that possesses short helix pitch and relatively large spontaneous polarization. The structure of the material is therefore a deformed helix ferroelectric (DHF) liquid crystal [17–19].
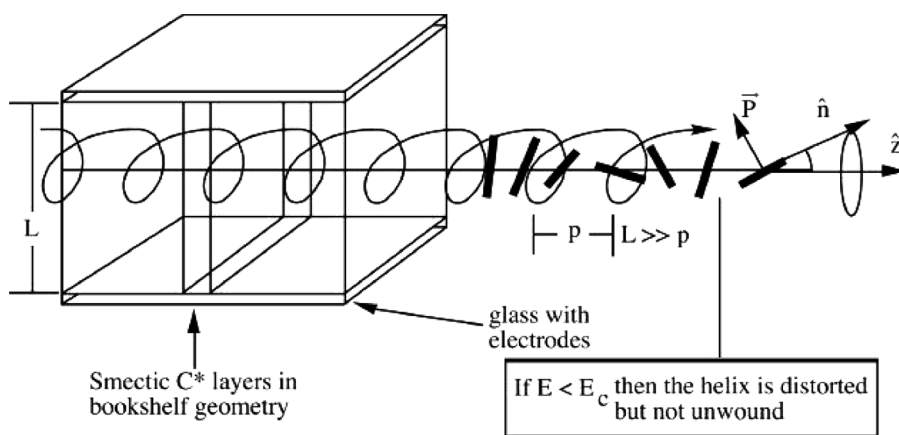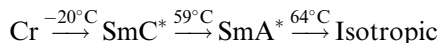

Figure 1. Helical structure of SmC* phase.

Experimental

The base liquid-crystal material used in the current experiment is ferroelectric mixture FLC-6304 (Hoffmann La Roche, Rolic, Switzerland). It exhibits ferroelectric SmC* (chiral smectic C) and SmA *phases. The corresponding transition temperatures are given by

$$\text{Cr} \xrightarrow{-20^\circ C} \text{SmC}^* \xrightarrow{59^\circ C} \text{SmA}^* \xrightarrow{64^\circ C} \text{Isotropic}$$

It has large spontaneous polarization ($110 \, nc/cm^2$), short pitch ($0.35 \, \mu m$), and large tilt angle (27°) [20]. The thermotropic mesomorphism and the transition temperatures of this material have also been confirmed by both the optical thermal polarizing microscopy and differential scanning calorimeter (Perkin-Elmer DSC-7, Mumbai, India).

The guest–host (G-H) mixtures of this liquid crystal were prepared by doping it with 1, 2, and 4% (wt/wt) concentration of Claussesn anthraquinone (CLU437730) blue dichroic dye (obtained from BDH Chemicals Ltd., Poole, UK). The dye was free from ionic impurities and had good solubility in the liquid crystal. These G-H mixtures were then filled in the planar cell of $5 \, \mu m$ thickness by the capillary action at their isotropic temperature. The dye imparted good coloration to the samples when compared with undyed host compound. The transition temperatures of these guest–host mixtures increased by about $6^\circ C$–$8^\circ C$ at T_{AI} (SmA* isotropic transition temperature) corresponding to 1, 2, and 4% dye concentrations, but no appreciable change in transition temperature was noticed at T_C (SmC*-SmA* transition temperature). The temperature of each sample was maintained at an accuracy of $0.1^\circ C$ in a programmable temperature controller coupled to hot stage (Linkam Scientific Instruments Ltd., Surrey, UK; TP94 and THMS600). The optical texture and alignment was observed on polarizing microscope (Olympus Model BX51P, Japan).

The electrical measurements were taken by a current reversal method using triangular and square waves. The output was taken on a Tektronix oscilloscope interfaced with a computer. The triangular and square waves used for these measurements were obtained from the Scientech function generator.

The dielectric parameters were measured in the frequency range of 50 Hz to 1 MHz, using an impedance analyzer (Fluke Model PM 6306, Everett, WA) interfaced with a computer. The cells were calibrated using air and benzene as standard reference media and stray capacitance was removed. The results were found to be reproducible.

Results and Discussion

Electrical Studies

A symmetric triangular wave of frequency $\sim$20 Hz and voltage sufficient for complete unwinding of the helix was applied to the liquid crystal sample to measure polarization. The total current across the resistance can be written as the sum of three terms; the capacitive term, the ionic conduction term, and the polarizing part. Polarization current is due to charge induced by the dipole realignment in the form of polarization. The hump of the polarization is directly associated with dipole reorientation. The area under the polarization hump gives the measure of polarization in
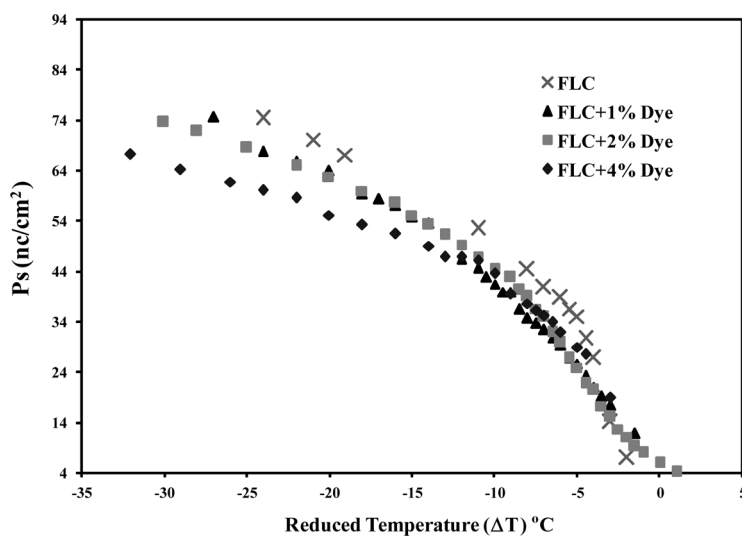
Figure 2. Reduced temperature vs. polarization plot for FLC and its G-H mixtures.

the sample. The square wave method was used for simultaneous measurement of polarization and response time. The temperature dependence of the polarization for pure mixtures and its G-H derivatives is shown in Fig. 2. It follows a typical trend in its variation with temperature represented by the power law. However, the polarization decreases with addition of dye in the SmC* phase and shows an increase near the transition to SmA* phase.

The variations of response time and rotational viscosity with temperature are shown in Figs. 3 and 4, respectively. The switching time of the pure material is found to be less than that of the dyed samples, whereas no appreciable change is observed in viscosity of the dyed samples.

Figure 3. Temperature dependence of response time for the FLC and its G-H mixtures.

Figure 4. Temperature dependence of rotational viscosity for the FLC and its G-H mixtures.

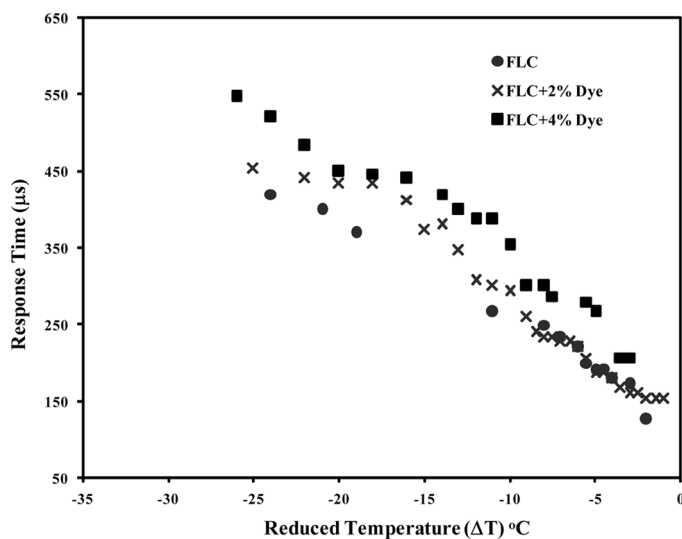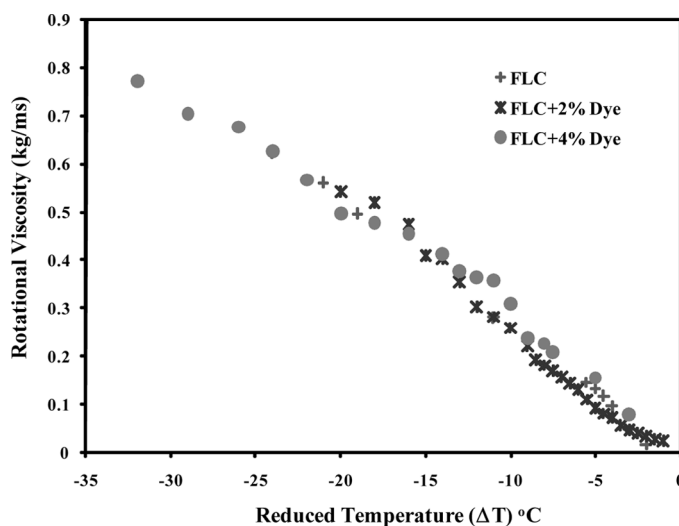## Dielectric Studies

The frequency dependence of the complex permittivity of pure and guest–host FLC mixtures in the SmC* and SmA* phases is shown in Figs. 5(a) and 5(b) and 6(a) and 6(b), respectively, clearly indicating the presence of single relaxation mode in both phases (GM in SmC* and SM in SmA*). We notice an overall decrease in permittivity in the SmC* phase with increase in dye concentration (Fig. 5), whereas it increases in the SmA* phase (Fig. 6). It is also seen that permittivity shows a slight change up to 2% of dye concentration but a noticeable effect is observed when the dye concentration is increased to about 4%. A comparison between ε' values in Figs. 5(a) and 6(a) reveals that ε_{SmC*} is about 12 times greater than the ε_{SmA*} for pure mixture as well as at lower dye concentrations (1% wt/wt), but this difference narrows down to about 6 times for 4% dye concentration.

The variation of complex permittivity as a function of reduced temperature ($\Delta T = T - T_C$) at different dye concentrations is shown in Figs. 7(a) and 7(b), respectively. It is seen that the ε' shows a small increase as we approach T_C but abruptly decreases to a very low value in the SmA* phase after attaining a hump at the transition. Permittivity depicts a decrease with increasing dye concentration in the SmC* phase followed by gradual inversion of effect of dye on permittivity in the vicinity of T_C. However, it is interesting to note an appreciable decrease of the permittivity in pure FLC mixture over dyed samples in the SmA* phase. A similar trend is observed for ε'' in Fig. 7(b).

The dielectric strength ($\Delta\varepsilon$) of the relaxation modes is calculated by fitting the experimental data in the form of Cole-Cole plot corresponding to the intersection of the semicircle with ε' axis. The temperature dependence of the dielectric strength of relaxation modes of the pure and G-H mixtures is shown in Fig. 8. In SmC* phase, the dielectric strength of GM decreases in G-H mixtures with slight inversion of effect near T_C. The dielectric strength of SM (SmA* phase), on the other hand,
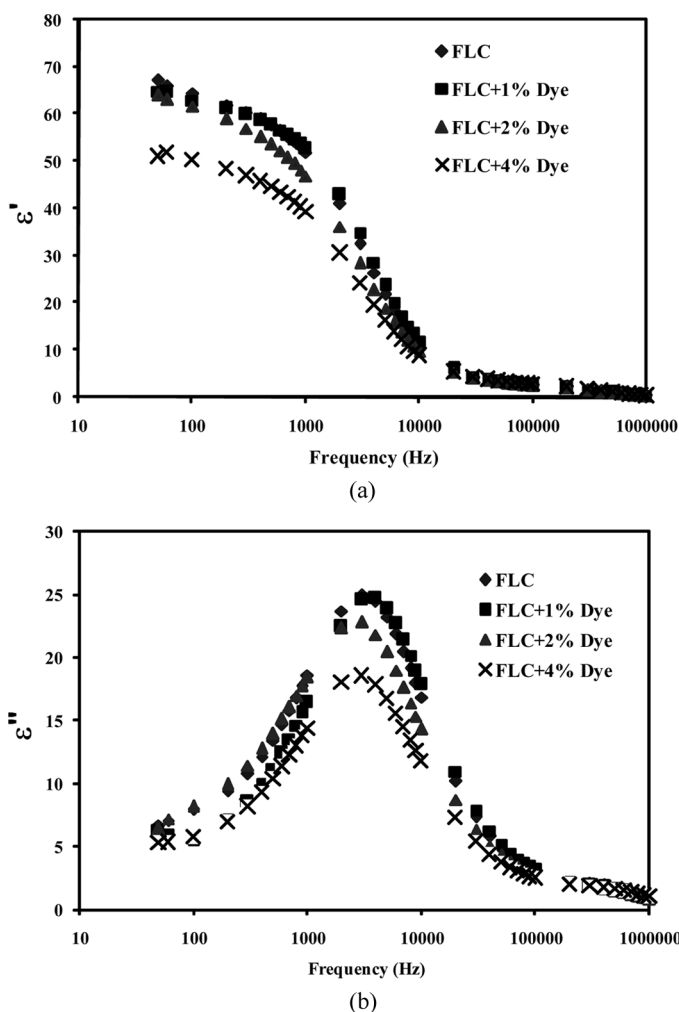
Figure 5. Frequency dependence of the (a) real and (b) imaginary part of complex permittivity in the SmC* phase ($\Delta T = -18°C$) for FLC and its G-H mixtures.

increases with dye addition. The temperature dependence of the relaxation frequency for GM and SM is shown in Fig. 9. The relaxation frequencies of the GM are not affected much by the addition of dye, whereas a decrease is observed for SM in the SmA* phase.

Theoretical Considerations and Discussions

Theory

SmC Phase.* The SmC* structure, in the relaxed state, is helicoidal (Fig. 1) and can be represented in terms of a one-dimensional model giving the azimuthal angle (ϕ) as a function of z along the helical axis, $\phi = qZ$ where $q = 2\pi/p$ is the wave vector of the helix pitch p. The ordering of the molecule in this phase can be given by the two
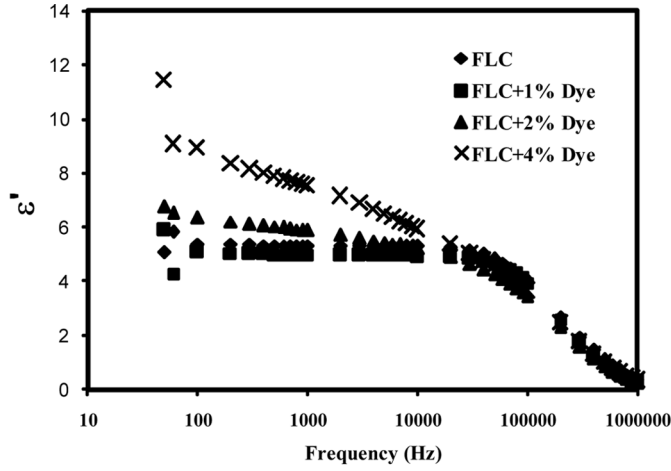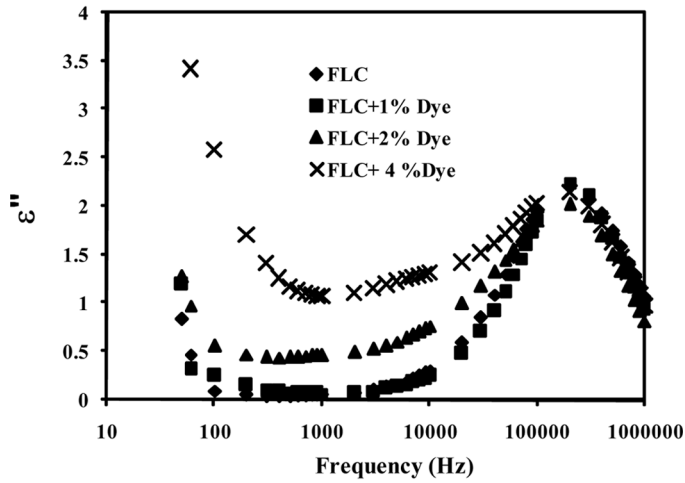
Figure 6. Frequency dependence of the (a) real and (b) imaginary part of complex permittivity in the SmA* phase ($\Delta T = 2°$C) for FLC and its G-H mixtures.

spatially modulated order parameters, $\xi(z)$ and P(z), representing the magnitude and direction of tilt angle (θ) and the polarization (P), respectively [21–25].

$$\xi(Z) = \theta[\hat{x}\cos\phi + \hat{y}\sin\phi]$$
$$P(Z) = P[-\hat{x}\cos\phi + \hat{y}\sin\phi]$$
$$(1)$$

If P from Eq. (1) is projected on a circle as a function of ϕ over a full period, we get isotropic distribution of P that gives no average polarization along the y-axis. An application of weak field in the y-direction results in anisotropic distribution of P yielding a net P_y component, given by [23–26]:

$$P = \varepsilon_0(\varepsilon_{\perp\infty} - 1)E + \varepsilon_0\Delta\varepsilon_G E \tag{2}$$
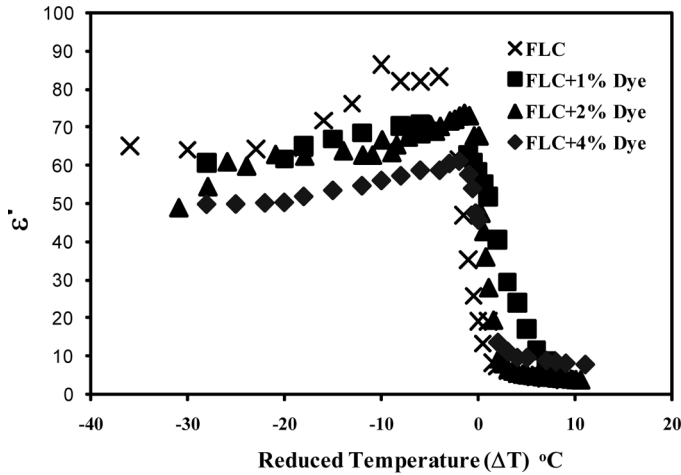
(a)
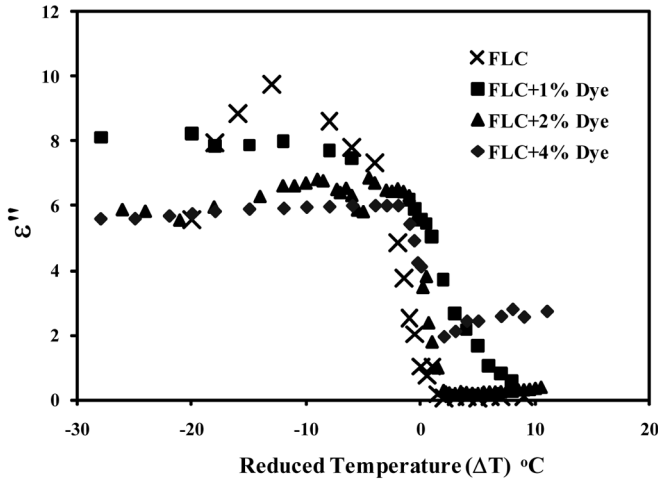
(b)

Figure 7. Temperature dependence of the (a) real and (b) imaginary part of complex permittivity for FLC and its G-H mixtures.

It is this component that is the origin of the Goldstone mode contribution to the dielectric constant ($\Delta\varepsilon_G$), the contribution due to linear deformation of helicoidally ordered P-vector [26]. When the helical structure is deformed and then allowed to relax, it comes back to the unperturbed state after a relaxation time τ_G due to the action of elastic torque and dissipative viscous torque. So, it is possible to calculate elastic constant (K_φ), rotational viscosity (γ_φ), and dielectric constant ($\Delta\varepsilon_G$) of Goldstone mode. Because well below transition temperature GM is the only mode contributing to dielectric permittivity, the dielectric parameters of GM are used to measure the viscosity as well as the complex permittivity (ε^*) of SmC* phase [27,28]. Starting from the viscoelastic
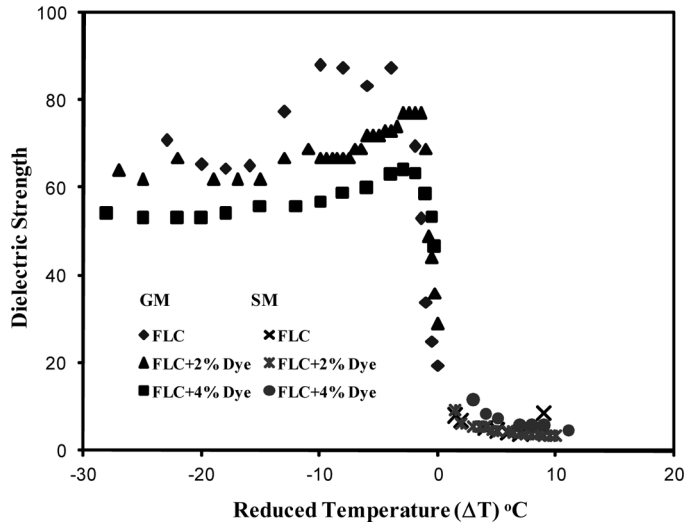
Figure 8. Variation of dielectric strength of GM and SM as a function of temperature for FLC and its G-H mixtures.

equation the relations of τ_G, $\Delta\varepsilon_G$, γ_φ, f_G (relaxation frequency), and hence ε^* are as follows [22,26,27]:

$$\tau_G = \frac{\gamma_\phi}{K_\phi q^2} \tag{3}$$

$$\Delta\varepsilon_G = \frac{P^2}{2\varepsilon_G K_\phi q^2 \theta^2} \tag{4}$$

Figure 9. Temperature dependence of relaxation frequency of GM and SM for FLC and its G-H mixtures.

$$\gamma_G = \gamma_\phi = \frac{P^2}{4\pi\varepsilon_o\theta^2(\Delta\varepsilon_G f_G)} \tag{5}$$

$$f_G = \frac{P^2}{4\pi\gamma_G\Delta\varepsilon_G\theta^2} = \frac{R_0}{4\pi\gamma_\phi} \tag{6}$$

$$\varepsilon^* = \varepsilon_\infty + \frac{\Delta\varepsilon_G}{1 + (i\omega\tau_G)^{1-\alpha_G}} \tag{7}$$

where α_G is distribution parameter and ratio R_0 is almost constant [29]. Equations (3)–(6) are also obtainable from generalized Landau model [30–32].
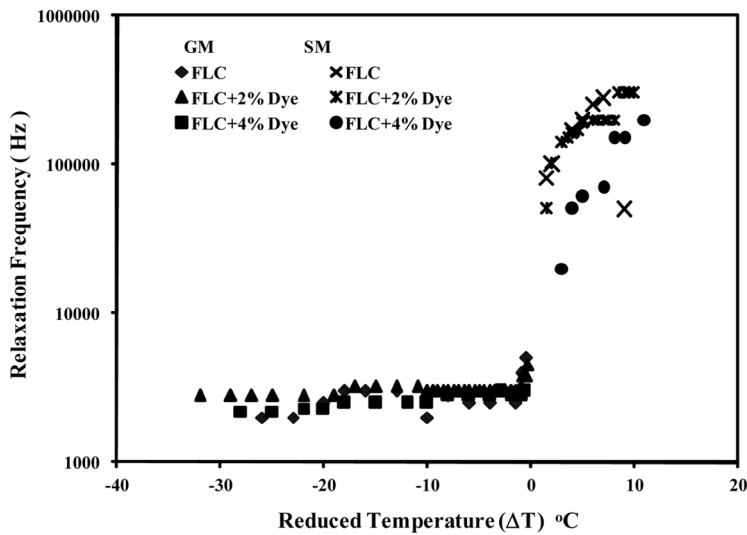
Equation (3), representing relaxation time, is, however, valid only up to the field of helix unwinding E_u [22,33]:

$$E_u \approx \frac{K_\phi q^2}{P_s}$$

For $E \geq E_u$, the equation reduces to [22,34,35]:

$$\tau_S = \frac{\gamma_\phi}{P_S E} \tag{8}$$

Here τ_S represents the time for switching of the molecule between two polarization states (parallel and antiparallel to the electric field) without the sample going to the helicoidal state. The time interval for this reorientation is called *switching time* and depends upon the polarization and the rotational viscosity. This equation is also used to measure rotational viscosity of SmC* phase using current reversal method that gives direct measurement of τ_S and P.

SmA* Phase. In SmA* phase phasons are degenerate and the contribution from the GM vanishes. Here, only amplitude fluctuations of tilt angle are present. The mode associated with these fluctuations is called soft mode. It appears in the vicinity of T_C and up to few degrees above in the SmA*.

Discussion

As discussed earlier, a decrease in polarization and increase in switching time is observed in the G-H mixture relative to the pure FLC, whereas rotational viscosity remains almost same. The polarization, according to Eq. (1), is related to pitch. Theoretically, pitch depends on chiral content of the SmC* phase. The dilution of the chiral content increases pitch, causing reduction of polarization with comparatively small effect on the rotational viscosity [22]. Our experimental observations on adding dye are in good agreement with the theory. In G-H mixtures, addition of the dye molecules to the host liquid crystal reduces the chiral content, thereby resulting in the decreased polarization (Fig. 2) and negligibly changed rotational viscosity (Fig. 4). The switching time becomes larger (Fig. 3) in the G-H mixture due to a decrease in polarization as clear from Eq. (8).

The reduction in the dielectric constant of the goldstone mode (Fig. 8) is expected as it depends on the square of polarization, which is decreasing (Eq. (4)). According to Eq. (7) this further decreases the permittivity of SmC^* as is observed in Fig. 5. The relaxation frequency of GM does not show much change in its value because it depends on the rotational viscosity, which is constant (Eq. (6)).

In SmA^* phase, only soft mode contribute to the permittivity. The transition from SmC^* to the SmA^* in G-H mixture (Fig. 7) seems to be less abrupt, increasing the tilt angle variation in SmA^* phase. The contribution of the soft mode increases simply due to the tilt angle variations. It further increases the complex permittivity of SmA^*phase (Fig. 6) and hence the dielectric strength (Fig. 8).

Conclusions

A detailed analysis of dielectric and electrical properties of pure and guest–host FLC has been carried out. Our results indicate that

- the dispersion of anthraquinone dye in the FLCs strongly influences the dielectric parameters and helix dynamics.
- the permittivity in the guest–host mixture is relatively low in SmC^* phase, whereas it increases in the SmA^* phase compared to pure material.
- the addition of dye results in the decreased value of spontaneous polarization in the SmC^* phase, whereas it increases near the transition to the SmA^* phase.
- a theoretical model has been presented to support our experimental results.

Acknowledgments

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