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Abstract. Dielectric properties of ferroelectric liquid crystalline mixture FLC-6980 and its anthraquinone dye (2% wt/wt) doped sample have been studied in SmC* and SmA phases in the frequency range from 100 Hz to 1 MHz in planar and homeotropic aligned cells. We observed the molecular relaxation mode in the homeotropically aligned cell at 33 °C at a frequency of 36 kHz in the SmC* phase. In the planar cells, goldstone and a new relaxation mode have been observed. A soft mode appeared in the vicinity of the SmC*–SmA transition. The dielectric increment, distribution parameter and relaxation frequency of these modes have been evaluated at different temperatures and bias voltages. Our results are in agreement with the extended Landau model.
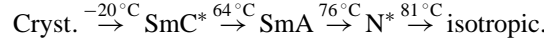
1. Introduction

Experimental and theoretical studies on ferroelectric liquid crystals in the chiral smectic C (Sm*C) phase have seen a tremendous growth during the past two decades. It is primarily due to their potential applications in fast electro-optic devices [1, 2]. The SmC* phase is a consequence of spatially modulated structure in which the azimuth angle of the long molecular axis precesses helicoidally around the smectic layer normal while going from one smectic layer to another. Levstik *et al* [3] explained that because of the molecular chirality, the dielectric responses of SmC* phase can be described by at least two relaxation processes, i.e. 'goldstone' and 'soft mode'. The dielectric studies of ferroelectric liquid crystals (FLCs) give information regarding molecular orientations and relaxation mechanism. A review of the literature [4–17] reveals that the dielectric spectroscopy and electro-optic properties of these materials has been studied extensively both theoretically and experimentally but there has been no effort to understand the effect of dichroic dyes on the dielectric relaxations in FLC systems.

   In this paper, we report on the effect of low concentration of anthraquinone (AQ) dye on the dielectric properties of a novel FLC mixture at 10 V external dc bias voltage. The measurements have been carried out in homogeneous (planar) and homeotropically aligned 7.5 μm cells over a wide frequency range (100 Hz–1 MHz). The Goldstone mode (GM) and soft mode (SM) have been observed in planar cells whereas the molecular mode appeared in a homeotropically aligned cell. The results will be discussed in section 3.

2. Experiment

Systematic studies of dielectric measurements have been carried out in a liquid crystalline material FLC-6980 (obtained from Hoffmann La Roche, Switzerland). The phase sequence

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of this mixture as observed through thermal polarizing microscopy and differential scanning calorimetry is given as:

$$\text{Cryst.} \overset{-20\,°C}{\to} \text{SmC}^* \overset{64\,°C}{\to} \text{SmA} \overset{76\,°C}{\to} \text{N}^* \overset{81\,°C}{\to} \text{isotropic.}$$

This material has low spontaneous polarization ($\sim$21.7 nC cm^{-2}) and tilt angle ($\sim$25°) and large pitch ($\sim$12–15 μm). The guest–host mixture (G–HM) was prepared by the dispersion of anthraquinone (AQ) dye at a concentration of about 2% wt/wt in the FLC-6980 (FM). The cells, consisting of conducting indium tin oxide (ITO) coated glass substrates, were procured from Lucid (UK) [18]. These cells have been pre-treated with polyimide coating to obtain planar alignment and with silane coating to obtain the homeotropic alignment. The cells of thickness 7.5 μm have been calibrated using air and benzene as standard references for calculating the absolute values of the dielectric permittivity. The cell was filled at the isotropic temperature of the liquid crystal and then cooled slowly at 0.2 °C min^{-1} in a hot stage–temperature programmer. We observed the appearance of chevron texture in the planar cells. This was avoided by applying a low frequency (up to 10 Hz) pulse at a voltage of $\sim$20 V$_{pp}$ in order to obtain a desired planar alignment. The dielectric measurements were carried out in these sample cells in both planar and homeotropic orientations separately. This alignment was confirmed visually through a Getner polarizing microscope under crossed polarizers.

The complete dielectric spectroscopy investigations of these samples were made using a Hewlett-Packard impedance analyser model HP 4192A in the frequency range of 100 Hz–1 MHz. The temperature of the sample was controlled and maintained at an accuracy of 0.1 °C in a Mettler temperature programmer (FP 5) and hot stage (model FP 52).

3. Results and discussion

3.1. Planar alignment

The director reorientation in an SmC* phase can be described in terms of the real ($\epsilon'_\perp$) and imaginary ($\epsilon''_\perp$) parts of the complex dielectric permittivity ($\epsilon^*_\perp$), which is given by

$$\epsilon^*_\perp = \epsilon'_\perp - \mathrm{i}\epsilon''_\perp. \tag{1}$$

In general, permittivity decreases with increase of the frequency for each mode at a given temperature. The dielectric increment of a given mode can be defined as

$$\delta\epsilon = \epsilon_{\perp 0} - \epsilon_{\perp\infty} \tag{2}$$

where $\epsilon_{\perp\infty}$ and $\epsilon_{\perp 0}$ are the high and low frequency limit of the dielectric permittivity. This quantity is related to the average induced polarization $\langle P \rangle$ of the corresponding mode by [6]

$$\epsilon_0 \delta\epsilon = \lim_{E\to 0} \frac{\langle P \rangle}{E} \tag{3}$$

where E is the magnitude of a static applied electric field and ϵ_0 the permittivity of free space. The temperature and frequency dependence of the complex permittivity of an FLC mixture evaluated using the Cole–Cole relation [4, 14,19–21] is given by

$$\epsilon^*_\perp = \epsilon_{\perp\infty} + \frac{\epsilon^{SM}_{\perp 0} - \epsilon^{SM}_{\perp\infty}}{1 + (\mathrm{i}\omega\tau_{SM})^{1-\alpha_{SM}}} + \frac{\epsilon^{GM}_{\perp 0} - \epsilon^{GM}_{\infty}}{1 + (\mathrm{i}\omega\tau_{GM})^{1-\alpha_{GM}}} + \frac{\epsilon^{NRM}_{\perp 0} - \epsilon^{NRM}_{\perp\infty}}{1 + (\mathrm{i}\omega\tau_{NRM})^{1-\alpha_{NRM}}} \tag{4}$$

where $\delta\epsilon^{SM}$, $\delta\epsilon^{GM}$ and $\delta\epsilon^{NRM}$ represent dielectric increments (i.e., $\delta\epsilon^i = \epsilon^i_{\perp 0} - \epsilon^i_{\perp\infty}$, where i is SM, GM and NRM) of the SM, GM and new relaxation mode (NRM) respectively. τ_{SM}, τ_{GM} and τ_{NRM} are relaxation times, whereas α_{SM}, α_{GM} and α_{NRM} represent distribution parameters of these modes respectively. The second term in equation (4) is connected to the SM while
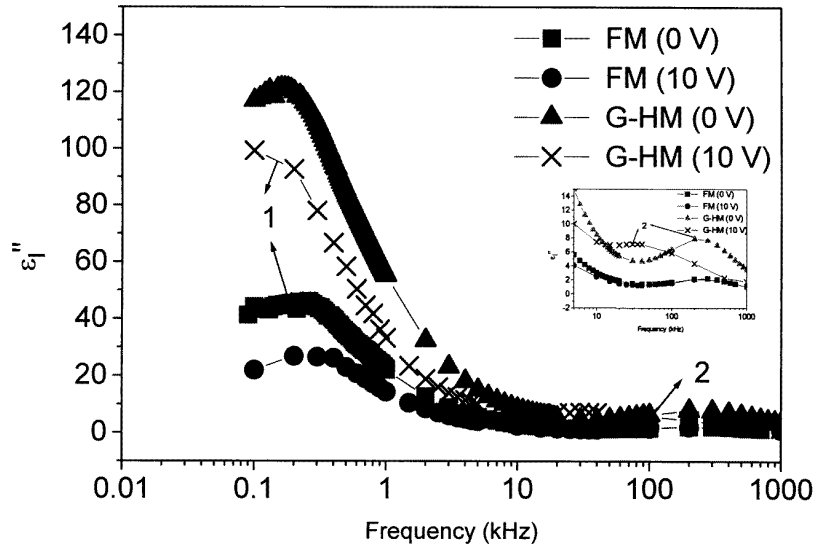
Figure 1. The frequency dependence of $\epsilon''_\perp$ for G–HM and FM at 0 and 10 V bias voltage in 7.5 μm cells.
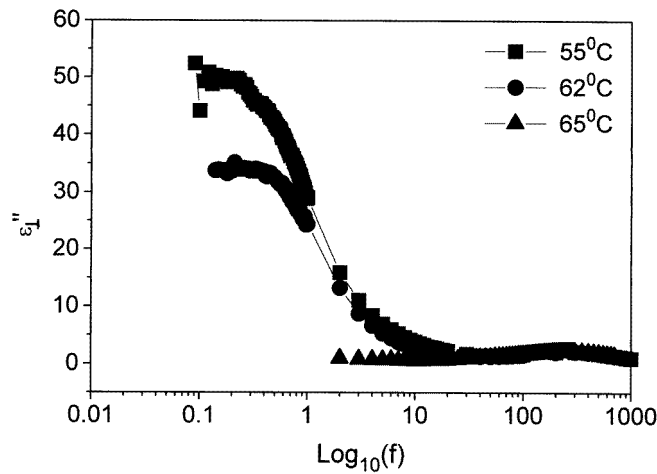
Figure 2. The frequency dependence of $\epsilon''_\perp$ for FM at different temperatures.

the third and fourth terms represent the GM and NRM respectively. Far from the SmC*–SmA transition (T_{C*A}) temperature in the SmC* phase there is a GM and NRM contribution, whereas near T_{C*A} GM and SM are dominant.

Figure 1 shows the variation of the imaginary part of the complex permittivity ($\epsilon''_\perp$) as a function of frequency at 0 and 10 V bias voltages for FM and G–HM. It is seen that they reflect two relaxation modes, GM and NRM (new relaxation mode), denoted by 1 and 2 respectively. This NRM could be formed due to the domain formation at the substrate surface. In the presence of an external bias the GM contribution is partially suppressed. It is clear that the bias field has no effect on the NRM in FM, while in G–HM the NRM shifted toward the lower frequency side under the application of field (see the inset of figure 1). This might be due to the

(a)

(b)
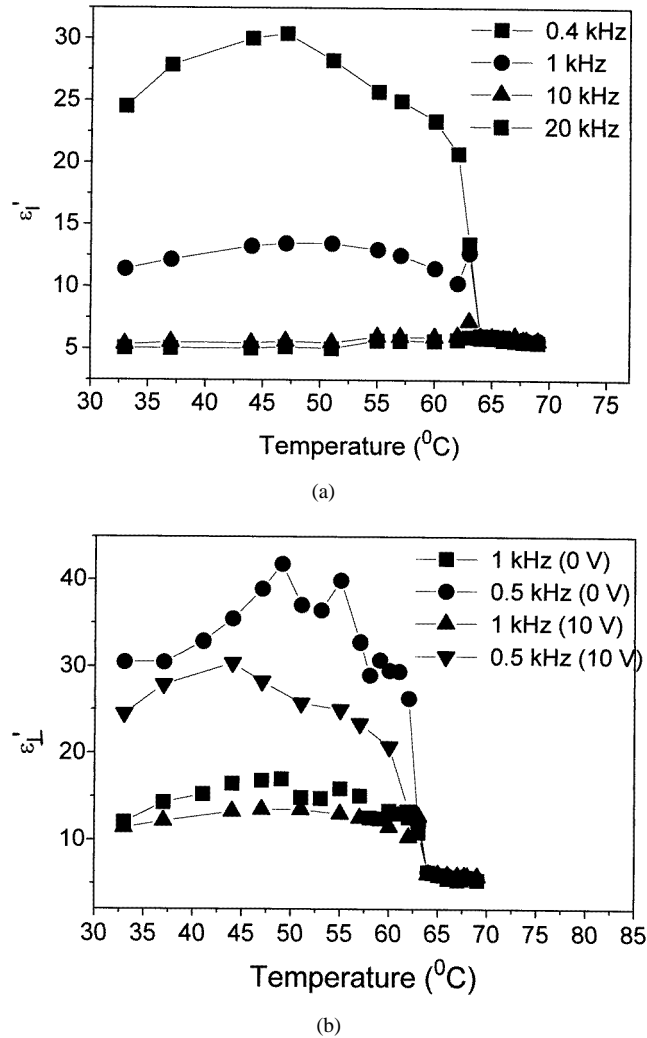
Figure 3. The temperature dependence of the permittivity of $\epsilon'_\perp$ (a) at different frequencies and (b) at 0 and 10 V bias voltages at different frequencies.

fact that the induced tilt is very small and as such there is no change in the elastic energy under the application of field. Frequency dispersion data have been analysed using equation (4).

The dielectric spectrum near the T_{C^*A} transition temperature is shown in figure 2. It is seen that below the transition temperature there is an absorption effect due to the GM and NRM. As we approach T_{C^*A}, it is noted that the GM contribution tends to vanish and the SM becomes dominant. This behaviour is reported in FLCs by other authors [4].

The variation of $\epsilon'_\perp$ versus temperature at different frequencies at 10 V is shown in figure 3(a). It is seen that the magnitude of $\epsilon'_\perp$ decreases with the increase of frequency and near T_{C^*A} it decreases sharply. Near T_{C^*A}, a small hump has been observed above 1 kHz. $\epsilon'_\perp$ versus temperature at 0.5 kHz and 1 kHz at selected bias voltages is shown in figure 3(b). It shows that the magnitude of the dispersion decreases with the field. This can be explained on the basis of the appearance of relaxation modes i.e. GM and SM. The magnitude of $\epsilon'_\perp$ decreases due to the suppression of the GM contribution under the application of the field.
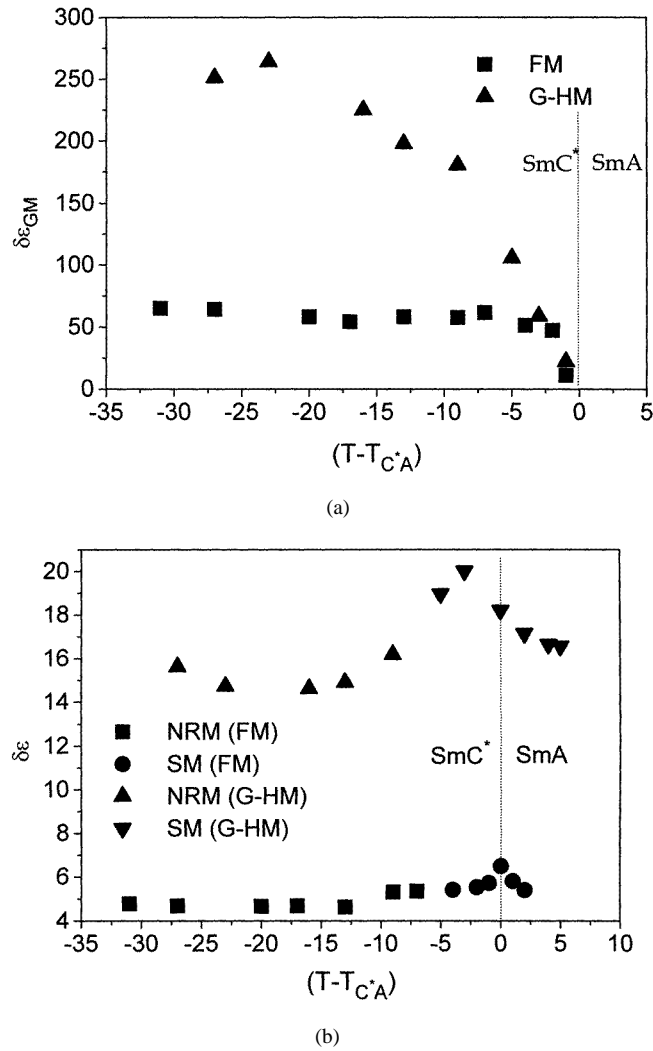
(a)

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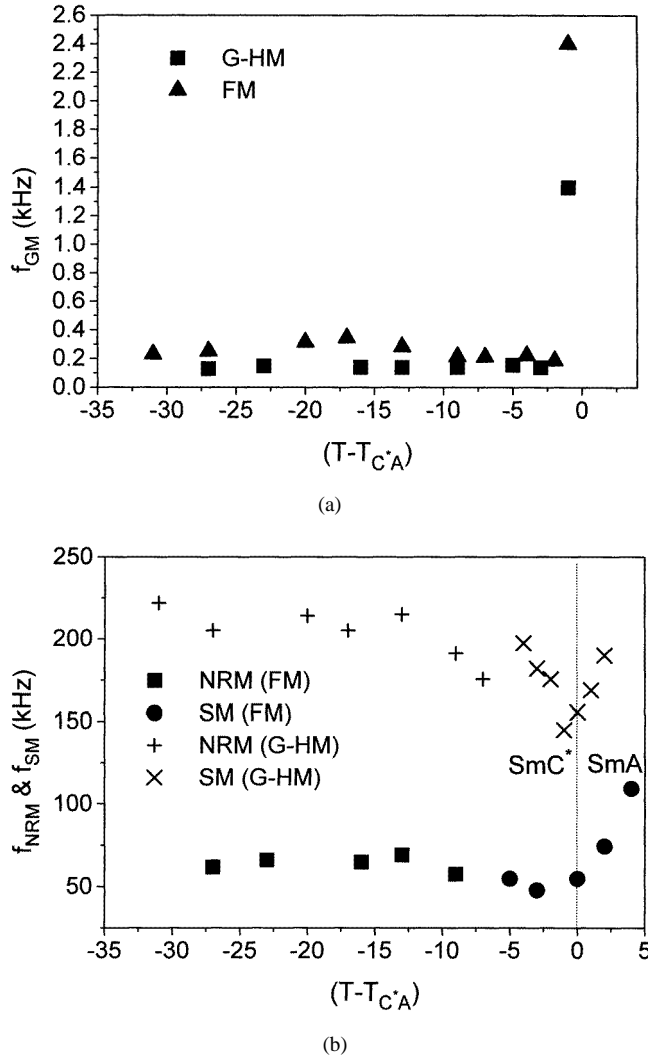
Figure 4. Goldstone mode relaxation frequency (f_{GM}) versus reduced temperature of (a) GM and (b) NRM and SM for FM and G-HM.

Relaxation frequency and dielectric increment of the GM (f_{GM}, $(\delta\epsilon)_{GM}$), NRM (f_{NRM}, $(\delta\epsilon)_{NRM}$) and SM (f_{SM}, $(\delta\epsilon)_{SM}$) have been evaluated for both the mixtures i.e. FM and G-HM. The relaxation frequencies of the GM, NRM and SM have been evaluated, and are shown in figure 4(a), (b). It is noticed that GM relaxation frequency is almost independent of temperature and increases near T_{C^*A}. According to the Landau model, the free energy density (f_d) in terms of polarization (P_0) and tilt angle (θ_0) in the unwound state under the application of an electric field is given by [23]

$$f_d = -\tilde{C} P_0 \theta_0 - \frac{\Omega P_0^2 \theta_0^2}{2} + \frac{P_0^2}{2\tilde{\epsilon}} - \frac{\eta P_0^4}{4} \tag{5}$$

where $\tilde{C}$, $\tilde{\epsilon}$, Ω and η are renormalized constants. The second term in equation (5) is due to the biquadratic coupling between polarization and the molecular tilt angle. The nature of the

Figure 5. Dielectric increment ($\delta\epsilon$) versus reduced temperature of (a) the goldstone mode (GM) and (b) NRM and SM for FM and G-HM.

bilinear ($\tilde{C}$) and the biquadratic coupling (Ω) can be understood by considering a parameter β given by

$$\beta = \frac{\tilde{C}\tilde{\epsilon}\eta^{1/2}}{\Omega^{1/2}}. \tag{6}$$

β is a dimensionless parameter and varies between 0 and 1. As we are using an FLC mixture of low spontaneous polarization a higher β value is expected which means that biquadratic coupling between polarization and tilt angle is less. Our experimental results indicate that the GM relaxation frequency is in agreement with the theory proposed by Carlsson *et al* [5] for a higher value of β.

The dielectric increment for GM, NRM and SM as a function of temperature is shown in figure 5(a), (b) for FM and G-HM. The temperature dependence of $\delta\epsilon_{GM}$ (figure 5(a)) results indicates a divergence in the $\delta\epsilon$ values in both the samples slightly away from the T_{C^*A}

transition while going into the SmC* phase. We observe that the G-HM shows an exponential increase in $\delta\epsilon$ with temperature and then tends to saturate beyond $\Delta T \sim -25\,°C$ whereas $\delta\epsilon$ does not show any variation beyond $\Delta T \sim -5\,°C$ in the FM sample. The dielectric increment predicted by the theoretical model [6] is given as

$$\delta\epsilon_{GM} \sim \frac{1}{2\tilde{K}_3\epsilon_0}\frac{P_0^2}{q^2\theta_0^2} \tag{7}$$

where $\tilde{K}_3$ is the renormalized elastic constant and q is the wavevector of the helix pitch. We see that $\delta\epsilon_{GM}$ does not depend on the sign of P_0; however the factor $(P_0/\theta_0)^2$ signifies a sharp decrease of $\delta\epsilon_{GM}$ near T_{C^*A}. A large value of $\delta\epsilon$ for G-HM can be explained on the basis of increase in the spontaneous polarization as predicted by equation (3).

In the vicinity of T_{C^*A}, SM dielectric parameters (f_{SM}, $(\delta\epsilon^{SM})^{-1}$) have been shown to vary linearly with temperature by considering the molecular field approximation according to the relation [9]

$$f_{SM} = a(T - T_{C^*A}) + b \tag{8}$$

where a and b are constants. As we know, the SM arises due to the fluctuations of the tilt angle in the vicinity of T_{C^*A}. Hence on approaching T_{C^*A}, an instantaneous tilt would arise due to the softening of the elastic energy. The variation of the induced tilt with temperature reflects a linear behaviour near T_{C^*A} for the SM whereas a non-Arrhenius behaviour is found for the NRM (figures 4(b) and 5(b)). Some authors have also reported a non-linear behaviour near T_{C^*A} for the SM [21, 24]

3.2. Homeotropic alignment

We have observed the collective modes i.e. GM and SM due to the director reorientation falling within the few hundred hertz and few hundred kilohertz range respectively. These modes contribute to the permittivity in the planar alignment, whereas the molecular reorientation around the short molecular axes in the homeotropic alignment gives rise to the molecular mode and its dielectric relaxation lies in the few kilohertz range. The dielectric spectrum for the homeotropic cell is shown in figure 6 in the form of a Cole–Cole plot [22]. The frequency
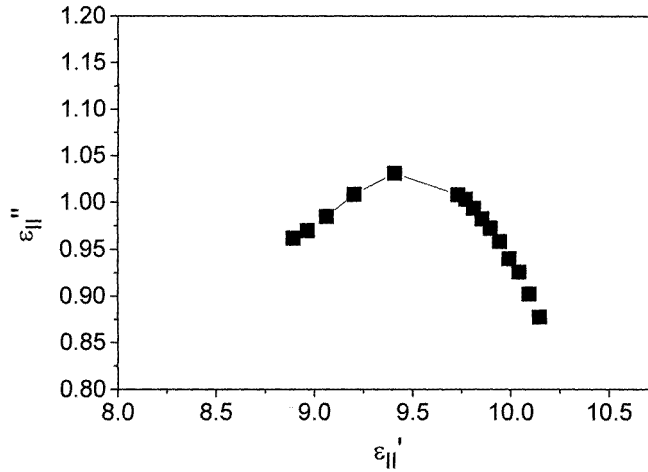
Figure 6. A Cole–Cole plot of the molecular mode for an FLC-6980 mixture in a 7.5 μm cell at 33 °C.

dependence of the complex permittivity connected with the reorientation of molecules about their short axes is given as

$$\epsilon_{\parallel}^{*} = \epsilon_{\parallel\infty} + \frac{\epsilon_{\parallel 0}^{M} - \epsilon_{\parallel\infty}^{M}}{1 + (i\omega\tau_{M})^{1-\alpha_{M}}} \tag{9}$$

where $\delta\epsilon^{M} = \epsilon_{\parallel 0}^{M}$-$\epsilon_{\parallel\infty}^{M}$ is the dielectric increment in this case. τ_{M} and α_{M} are the relaxation time and distribution parameter respectively. The dielectric increment and the relaxation frequency calculated for the molecular mode are given in table 1. The relaxation frequency of the molecular mode increases with the increase of the temperature. This is in conformity with the results reported by other authors [4].

3.3. Dielectric anisotropy

The variation of $\Delta\epsilon$ ($\Delta\epsilon = \epsilon_{\parallel} - \epsilon_{\perp}$) as a function of frequency in the SmC* phase at 51 °C is shown in figure 7. It is seen that below 1 kHz, the dielectric anisotropy is negative. This might be due to the transverse permanent dipole moment components in the molecular structure of the sample. It is seen that the magnitude of $\Delta\epsilon$ shows a marginal decrease with decreasing

Table 1. Dielectric parameters of the molecular mode at different temperatures.

Temperature (°C)	τ (μs)	$\delta\epsilon_{M}$	α^{M}
33	4.31	3.5	0.344
37	2.9	3.85	0.402
44	0.59	5.5	0.482
47	0.512	5.7	0.421
51	0.325	5.7	0.402
57	0.286	5.7	0.338
60	0.266	5.9	0.353
62	0.234	5.9	0.303
63	0.203	6.3	0.303
64	0.136	10.0	0.212
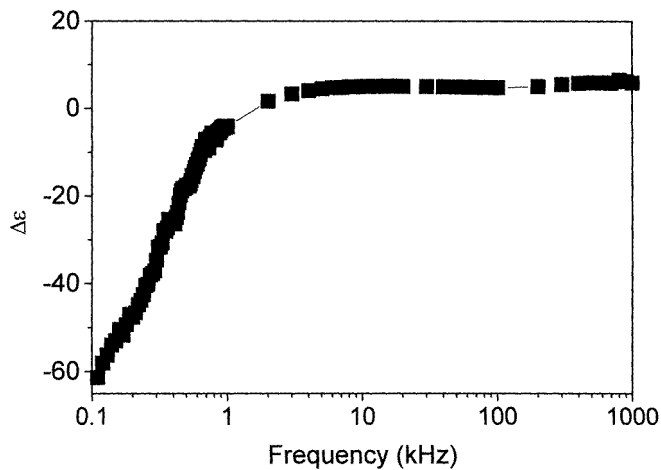
Figure 7. The frequency dependence of the dielectric anisotropy ($\Delta\epsilon$) at 51 °C.

frequency. This behaviour is due to the increase of the goldstone contribution to the $\epsilon_\perp$ component with decreasing frequency up to 2 kHz. $\Delta\epsilon$ is almost constant in the high frequency region beyond about 1.5 kHz. The changes in the sign of $\Delta\epsilon$ above 1 kHz by indicates the strong frequency dependence of various modes.

4. Conclusions

(i) In homogeneous alignment for FLC-6980 and guest–host mixture, contributions to the permittivity arise from the GM and small contributions from the NRM. Both modes show a non-Arrhenius type behaviour of relaxation frequency. Near the transition, the GM contribution decreases drastically. The SM parameter varies linearly with temperature and obeys the Curie–Weiss law. Our dielectric results are in agreement with the extended Landau model for a higher value of β.

(ii) In homeotropic alignment, the contribution to the permittivity arises from molecular mode and its relaxation frequency is 36 kHz at 33 °C temperature. The relaxation frequency of the molecular mode varies linearly with the temperature.

(iii) In GHM, the NRM shifts towards the low frequency side under application of field. This might be due to lowering of the flexibility of the molecule in the mixture and the effect of induced tilt.

(iv) $\Delta\epsilon$ is negative below 1 kHz. This probably indicates a strong frequency dependence. Moreover, experiments are in progress to explore the possible reason.

Acknowledgments

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