Dielectric relaxation and rotational viscosity of a ferroelectric liquid crystal mixture

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The dielectric permittivities have been measured over a wide temperature range of a ferroelectric liquid crystal mixture having low spontaneous polarization in its smectic-C^* (Sm-C^*) and smectic-A (Sm-A) phases on planar alignment. The measuring electric field is parallel to the layer plane. In this particular geometry of the cell, the well-known Goldstone relaxation mode has been observed in the Sm-C^* phase. Due to very low spontaneous polarization of molecules of this sample, we could not observe any soft mode in the Sm-C^* phase even very near the Sm-C^*–Sm-A transition temperature. The soft mode, however, is observed at the transition and a few degrees above the transition temperature. In addition to the soft mode and the Goldstone mode, we have observed another high frequency relaxation mode in both smectic phases. The dielectric strength as well as the corresponding relaxation frequencies of the modes have been calculated. The Goldstone mode rotational viscosity has been determined using evaluation models from dielectric results.
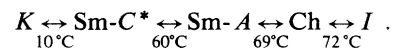
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I. INTRODUCTION

During the past several years, a tremendous growth in research, both theoretical and experimental, has been seen in the area of ferroelectric liquid crystals, after their discovery by Meyer et al. [1]. In this context, the study of the dielectric response of ferroelectric liquid crystal materials in the smectic-C^* (Sm-C^*) and smectic-A^* (Sm-A) phases is very important from both basic and technical points of view. Dielectric relaxation studies on a large number of ferroelectric liquid crystals have been recently reported, from which we can get an idea about the molecular orientation and relaxation mechanisms [2–11]. The chiral ferroelectric smectic-C^* phase is the consequence of a spatially modulated structure. The tilt angle (θ) of the long molecular axis with the smectic layer normal precesses helicoidally from one smectic layer to another. Because of the chirality of the molecules in the smectic-C^* phase, the dielectric behavior of this phase can be described by two relaxation processes [2]. The dominant Goldstone mode appears due to the phase fluctuation, i.e., the fluctuation of the azimuthal angle of the director around the helical axis, whereas the soft mode is due to the tilt fluctuation of the director.

For the purpose of applying ferroelectric liquid crystals to electro-optic devices, we should get the optimum values of spontaneous polarization, tilt angle, pitch, and relaxation frequency of the Goldstone mode. The electro-optic effects in the Sm-C^* phase is based on the field induced change of the azimuthal angle on a Sm-C cone, i.e., the Goldstone mode. So it is very important to study the dielectric response of the ferroelectric liquid crystals to obtain the contributions of both the soft mode

and the Goldstone mode accurately and to determine their relaxation frequencies and amplitudes as a function of temperature. The rotational viscosity is an important physical parameter that influences the switching time in the Sm-C^* phase. The rotational viscosity in the Sm-C^* phase was determined by an optical method [12] in a thin cell. The rotational viscosity of the Goldstone mode was measured by Levstik et al. from the dielectric measurement [13,14] in a thick sample.

In this paper we have reported the complete dielectric relaxation studies on a ferroelectric liquid crystal mixture, Merck ZLI-4655-000, obtained from E. Merck. The rotational viscosity has also been determined from dielectric measurement. The sample possesses low spontaneous polarization ($=7$ nC cm^{-2} at 20 °C). The phase sequences of the samples are as follows (Ch denotes cholesteric, I isotropic, and K crystal)

$$K \underset{10\,°C}{\leftrightarrow} \text{Sm-}C^* \underset{60\,°C}{\leftrightarrow} \text{Sm-}A \underset{69\,°C}{\leftrightarrow} \text{Ch} \underset{72\,°C}{\leftrightarrow} I \ .$$

II. EXPERIMENT

The ferroelectric liquid crystal (FLC) samples were held between two conducting glass plates whose surfaces had been treated properly for obtaining planar alignment. We have used two different pairs of cells, one of which is made of indium–tin oxide coated glass plates having a separation of 6 μm and the other one made of gold coated glass plates having a cell thickness of 17 μm. The sample was heated to its isotropic phase by Mettler Hot Stage (model FP 5) and then cooled down very slowly (0.2 °C/min) to room temperature. The temperature of the sample was stabilized to an accuracy of ±0.01 °C. A Hewlett-Packard impedance analyzer HP 4192A working in the frequency range of 5 Hz to 13 MHz was used for the complex dielectric permittivity measurements. Before putting the sample into the cells, the air capacitances for the two cells were recorded at different temperatures

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and with different frequencies. In the present study, the FLC mixture has a very low P_S value, so we could not excite the Goldstone mode with low ac measuring voltage. A measuring voltage of 1 V was applied in a direction parallel to the smectic layers. The stray capacitance for each cell was measured by using spec-pure benzene.

III. THEORETICAL BACKGROUNDS

The well-known formula for the complex dielectric constant is written as

$$\epsilon^*(\omega, T) = \epsilon'(\omega, T) - j\epsilon''(\omega, T) , \tag{1}$$

where $\omega = 2\pi f$ is the angular frequency of the applied electric field and T is the temperature of the sample. The real (ϵ') and imaginary (ϵ'') parts of ϵ^* can be determined from the measurements of capacitance C and conductance G of the sample.

In chiral Sm-C^* molecules, there are two relaxation modes connected with the reorientation of the director, two polarization modes connected with the fluctuation of the polarization order parameter, and one mode connected with the distortion of electronic arrangements. The difference between the low and high frequency contribution of the mode to the total dielectric constant is called the dielectric strength $\Delta\epsilon_i(T)$ of the mode. The relaxation frequencies of the two polarization models of around 500 MHz, reported by Benguigui [15], are beyond the range of the present experimental setup. In the smectic-C^* phase both the amplitude and phase fluctuations of the director are present. The complex dielectric constant is therefore written as

$$\epsilon^*(\omega, T) = \Delta\epsilon_G(T)/\{1 + (j\omega\tau_G)^{1-\alpha}\}$$
$$+ \Delta\epsilon_S(T)/\{1 + (j\omega\tau_S)^{1-\alpha}\} + \epsilon_\alpha , \tag{2}$$

where $\tau_i = 1/(2\pi f_i)$, the relaxation time of the corresponding mode, ϵ_α has the contribution from both the polarization modes and all other high frequency modes, and α is the distribution parameter.

In the smectic-A phase, only the tilt fluctuation of the director is present, and there is no contribution due to the phase fluctuation. The complex dielectric constant can then be written as

$$\epsilon^*(\omega, T) = \Delta\epsilon_{SA}(T)/\{1 + (j\omega\tau_{SA})^{1-\alpha}\} + \epsilon_\alpha , \tag{3}$$

where $\Delta\epsilon_{SA}$ is the dielectric strength of the smectic-A soft mode, while τ_{SA} is the corresponding relaxation time.

When the helical structure of the smectic-C^* phase is perturbed, it comes back to its unperturbed state with a certain relaxation time τ_G due to the elastic torque, and it is counteracted by the dissipative viscous torque. When an electric field E is applied for creating a torque in the smectic-C^* phase, the viscous elastic equation can be written as [8]

$$K_\phi \sin^2\theta \delta^2\phi/\delta Z^2 - \gamma_\phi \sin^2\theta \delta\phi/\delta\epsilon = PE\sin\theta . \tag{4}$$

K_ϕ contains the contribution from the bend (K_2) and

twist (K_3) elastic constants in the smectic-C^* phase and is given by

$$K_\phi = K_3\cos^2\theta + K_2\sin^2\theta . \tag{5}$$

The following expression relates the dielectric strength $\Delta\epsilon_G$ and relaxation frequency f_G in the Sm-C^* phase to the spontaneous polarization P and tilt angle θ,

$$\Delta\epsilon_G = P^2/(2\epsilon_0 K_\phi q^2\theta^2) , \tag{6}$$

$$\tau_G = \gamma_\phi/(K_\phi q^2) = 1/(2\pi f_G) , \tag{7}$$

where q is the magnitude of the wave vector of helical pitch, γ_ϕ is the rotational viscosity in the Sm-C^* phase, and ϵ_0 is the dielectric permittivity of the free space.

By solving Eqs. (6) and (7), γ_ϕ and K_ϕ may be written as

$$\gamma_\phi = \frac{1}{4\pi\epsilon_0} \frac{P^2}{\theta^2(\Delta\epsilon f_G)} , \tag{8}$$

$$K_\phi = \frac{1}{2\epsilon_0\Delta\epsilon_G}(P/q\theta)^2 . \tag{9}$$

IV. RESULTS AND DISCUSSIONS

The frequency and temperature dependence of the complex dielectric constant for the ferroelectric liquid crystal mixture has been studied far from the Sm-C^*–Sm-A phase transition, which is 60 °C in the present case as well as a few degrees above the phase transition temperature in the Sm-A phase. Figure 1 shows the Cole-Cole diagram for the Goldstone mode, i.e., the plot of dielectric loss (ϵ'') against dielectric permittivity (ϵ') at different temperatures in the Sm-C^* phase. For the single relaxation process, we expect to get a semicircle of the Debye type. However, from the figure it is observed that the curves are not exactly semicircular but consist of an arc of a circle with the center of the circle a little below the ϵ' axis with a very small distribution of relaxation times. One of the reasons for this type of distribution arises in a liquid crystal mixture when the components of the mixture have different sizes, and the
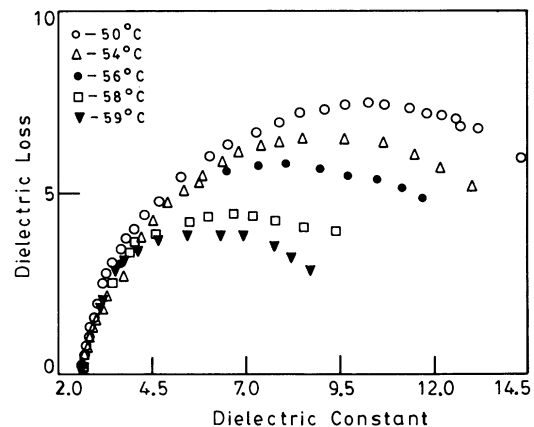

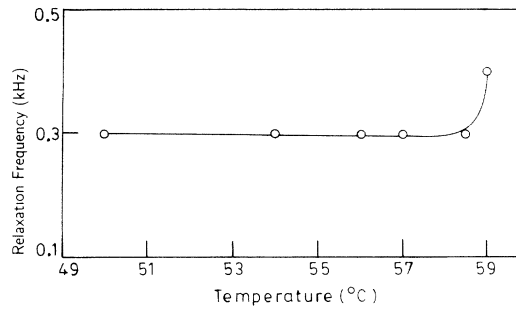FIG. 1. Cole-Cole plots for the Goldstone mode at different temperatures.

FIG. 2. Variation of relaxation frequency of the Goldstone mode with temperature.

FIG. 3. Temperature dependence of the relaxation frequency of the unknown mode.

other reason may be due to the absence of perfect alignment, which may create a defect structure. The distribution parameter that is very near the transition temperature attains a significant value; this may be due to the superposition of the contribution from both the soft mode and the Goldstone mode. Normally, the dielectric strength of the soft mode gradually decreases as $T_C - T$ increases in the Sm-C^* phase. In the present study, the spontaneous polarization (P_S) value of the liquid crystal mixture is very small, and we cannot observe the soft mode in the Sm-C^* phase. The relaxation frequency of the Goldstone mode, shown in Fig. 2, slowly increases with the increase of temperature. Very near transition, the Goldstone mode frequency is about 400 Hz. According to the Landau model, the free energy density (g) can be expressed in terms of the tilt angle (θ) and the polarization (P_S) in a state unwound by an external field [12] as

$$g = -\bar{C}P\theta - \Omega P^2\theta^2/2 + P^2/(2\bar{\epsilon}) + \eta P^4/4 , \qquad (10)$$

where $\bar{C}$, $\bar{\epsilon}$, Ω, and η are the renormalized constants. The Ω term commonly known as the biquadratic coupling term, has been introduced due to coupling between the tilt and polarization in the free energy density. For obvious reasons, the biquadratic coupling is less in our studied liquid crystal molecules due to a very low value of the spontaneous polarization. From Eq. (10), Urbanc and Zeks [12] have defined a dimensionless parameter β, such as

$$\beta = \eta^{1/2}\bar{\epsilon}\bar{C}/(\Omega^{1/2}) . \qquad (11)$$

The small β means more important biquadratic coupling. In our case, the β term should be comparatively higher because of the low P_S value of the FLC mixture. So the temperature dependence of the Goldstone mode relaxation frequency curve of the ZLI-4655-000 mixture in the present case corresponds well to that of the theoretically calculated curve of the higher β term [16].

In planar geometry of the cell, we should get the director mode due to tilt and phase fluctuations of the direction; and the polarization mode, which is expected to be observed in the frequency range of 500 MHz, is beyond our measurement facility. As the present FLC mixture has low spontaneous polarization, we have not observed the soft mode in the Sm-C^* phase. So in the Sm-C^* phase in the present study, we should get only the Gold-
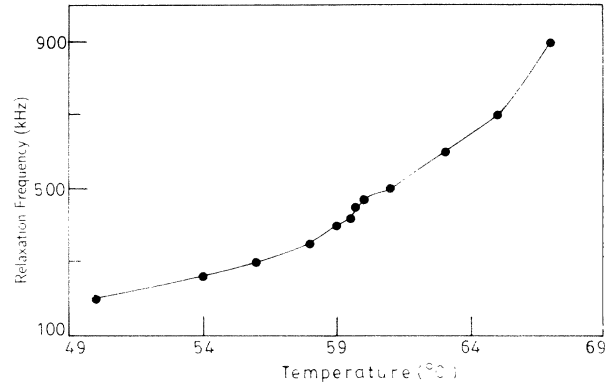
stone mode, due to phase fluctuation of the director, but surprisingly we have gotten another absorption region, which is around 80 kHz at 10 °C below the Sm-C^*-Sm-A transition, and it increases with the increase of temperature in the Sm-C^* phase. This unknown mode also exists in the smectic-A phase, and the relaxation frequency increases with temperature. So it may be concluded that this unknown mode is not related to the helical structure of the molecules. We have also made the dielectric relaxation studies for this FLC mixture in a homeotropically aligned cell. The relaxation frequency for that particular orientation of the FLC mixture is due to the rotation of the molecules around its short axis, and the relaxation frequency of this molecular mode is found to increase with temperature both in the Sm-C^* and Sm-A phases, as shown in Fig. 3. It is found that the relaxation frequency of the unknown mode, which was observed in the planar geometry of the cell, is very nearly equal the relaxation frequency of the molecular mode, which is observed in the homeotropic orientation of the sample. Moreover, we could not observe the unknown mode in the 6-μm PVA coated planar aligned cell. We observed it only on a 17-μm gold plated cell where no aligning agent was used. In our opinion, the unknown mode seems to be the molecular mode that arises due to the imperfect alignment of the sample. We were not able to measure the soft mode 2 °C above the transition temperature. The soft mode relaxation frequency sharply increases from 20–90 kHz, which was generally observed by other workers [6,7]. The Cole-Cole plot for the soft mode in the smectic-A phase and that of the unknown mode are shown in Figs. 4 and 5, respectively. The temperature dependence of the relaxation frequencies of the soft mode and the unknown mode is displayed in Fig. 6.

Theoretically, the temperature dependence of the Goldstone mode dielectric strength is shown in Eq. (6). From Eq. (6), it is expected that the Goldstone dielectric strength [6]

$$\Delta\epsilon_G \propto \frac{P^2}{k_3 q^2\theta^2} .$$

We have calculated the P/θ value (Fig. 7) from the data sheet of Merck Ferroelectric Liquid Crystals, and it is ob-
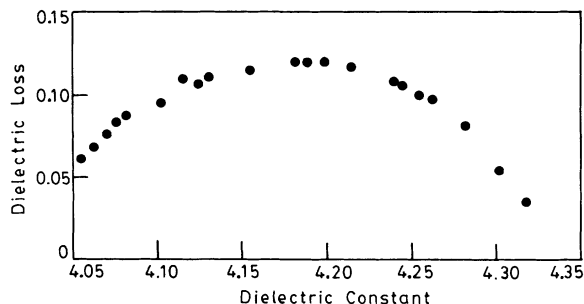
FIG. 4. Cole-Cole plots of the soft mode in the Sm- A phase at $T = 60.1\,°C$.

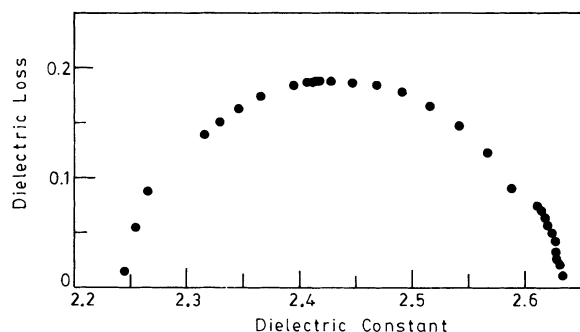
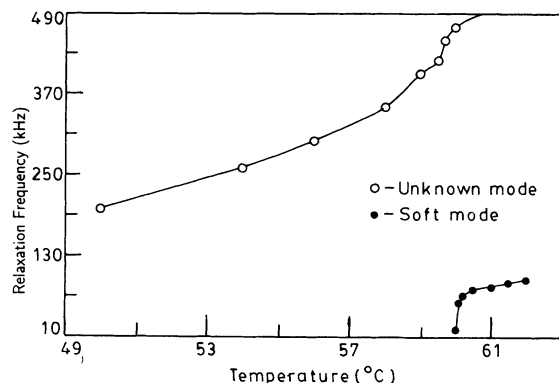FIG. 5. Cole-Cole plots of the unknown mode at $T = 60\,°C$.

FIG. 6. Variation of the relaxation frequency of the soft mode in the Sm- A phase and that of the unknown mode with temperature.
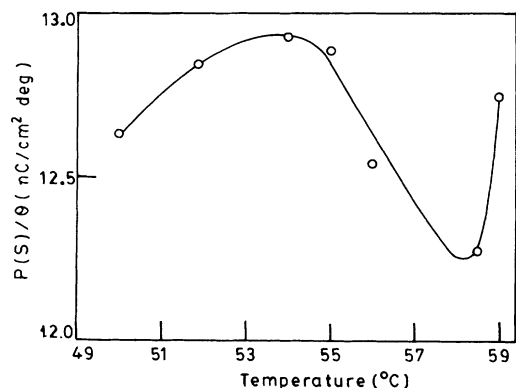

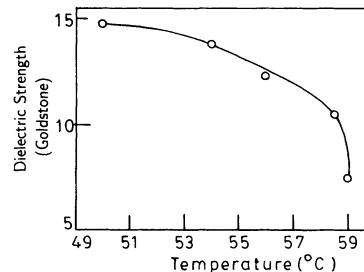FIG. 7. Variation of $P(S)/\theta$ in the smectic- C^* phase with temperature.

FIG. 8. Temperature dependence of the Goldstone dielectric strength $(\Delta\epsilon_G)$.

served that, as the temperature decreases, P/θ increases sharply and attains a saturated value further away from the T^*_{CA}. The ferroelectric pitch for the FLC mixture is generally high and varies slowly with $T_C - T$. Assuming the same slowly varying pitch with temperature as that observed by Carlsson *et al.* for DOBAMBC [17], the temperature dependence of the Goldstone mode dielectric strength in the present study also behaves in the same way, as is expected from Eq. (6), shown in Fig. 8. The magnitude of the dielectric strength, of course, depends on the value of spontaneous polarization and cell thickness. In the present study, both the cell thickness and P_S are very small, and for obvious reasons the dielectric strength $\Delta\epsilon_G$ in the Sm- C^* phase is smaller in comparison to the other reported values [7]. As the temperature cools down in the smectic- A phase, the soft mode dielectric strength $\Delta\epsilon_{SA}$ shown in Fig. 9 increases slowly from 2 °C above the Sm- A –Sm- C^* transition temperature, and from 0.5 °C above the transition temperature it increases very sharply to a maximum value at T^*_{CA}. The soft mode contribution arises due to the fluctuation of an instantaneous tilt in the smectic- A phase. As the temperature gradually decreases in the smectic- A phase, and when it comes near the Sm- C^* –Sm- A transition, an instantaneous tilt develops due to the softening of elastic energy, and it diverges at the transition temperature, as a result of which a permanent tilt in the smectic- C^* phase is generated. The temperature dependence of the instantaneous tilt that causes the soft mode behavior might develop in the same manner as that of the soft mode dielectric strength behavior with temperature.

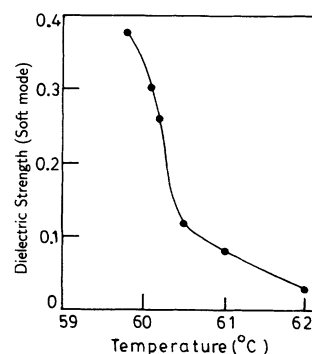The Goldstone mode rotational viscosity (γ_ϕ) for this

FIG. 9. Temperature dependence of the soft mode dielectric strength in the Sm- A $(\Delta\epsilon_{SA})$ phase.

FLC material, calculated using relation (8), is shown in Fig. 10 and corresponds fairly well to the γ_ϕ value obtained by the optical method [18] near the transition temperature. As we see from the figure, the rotational viscosity starts increasing with temperature very slowly from 10 °C below the Sm-C^*-Sm-A transition temperature, and near the Sm-C^*-Sm-A transition it increases sharply. Most of the reported values of the rotational viscosity γ_ϕ for a ferroelectric liquid crystal system decrease with the increase of temperature in the Sm-C^* phase [13,14]. But recently, Srivastava et al. [11] also reported that γ_ϕ of their system decreases slightly with temperature and then begins to increase with temperature up to T_{CA}^*. A 6-μm-thick cell has been used by us as well as by Srivastava et al. for dielectric measurement. On the other hand, the other workers have generally used cells of cell thickness ranging from 50–100 μm [13,14]. In a thin cell of 6 μm thickness, the Goldstone mode is suppressed sufficiently. So the Goldstone mode dielectric strength $(\Delta\epsilon_G)$ is also reduced sufficiently, particularly near the Sm-C^*-Sm-A transition. In the determination of γ_ϕ, $\Delta\epsilon_G$ involves the denominator of Eq. (8); this not
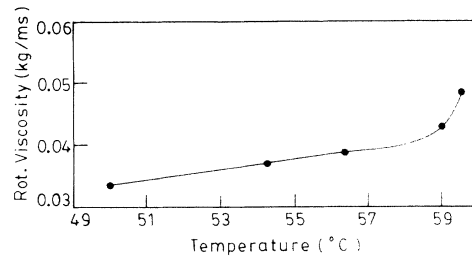

FIG. 10. Plot of the Goldstone mode rotation viscosity (γ_ϕ) vs temperature.

only increases the value but also causes the sudden rise of the Goldstone mode rotational viscosity γ_ϕ near T_C.

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