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A sub-hertz frequency dielectric relaxation process in a ferroelectric liquid crystal material

A. M. BIRADAR*, D. KILIAN, S. WROBEL† and W. HAASE
Institut fur Physikalische Chemie, Technische Universität Darmstadt,
Petersenstr. 20, 64287 Darmstadt, Germany

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Dielectric studies of the first order phase transition of a ferroelectric liquid crystal material having the phase sequence chiral nematic to smectic C* have been performed using thin (2.5 μm) cells in the frequency range 0.01 Hz to 12 MHz. For planar alignment, one of the cell electrodes was covered with a polymer and rubbed. Optically well defined alignment was obtained by applying an a.c. field below the N*–SmC* transition. Charge accumulation was enhanced by depositing a thick polymer aligning layer for the alignment of the liquid crystal molecules. A sub-hertz frequency dielectric relaxation process is detected in smectic C*, in the chiral nematic and a few degrees into the isotropic phase, due to the charge accumulation between the polymer layer and the ferroelectric liquid crystal material. The effect of temperature and bias field dependences on the sub-hertz dielectric relaxation process are reported and discussed.

1. Introduction

Ferroelectric liquid crystals have been studied extensively due to both their large electro-optic effects, which make them appear promising for optical displays, and their interesting basic properties [1]. Ferroelectric liquid crystals (FLCs)—due to their fast switching response—have a big advantage over nematics used in displays. However, they are not widely used in devices because there are a number of difficulties in their applications, including the understanding and control of alignment, switching mechanisms, etc. Various techniques [2, 3] have been used for aligning the FLC molecules other than the well known technique of polymer rubbed surfaces. The use of rubbed polymers is however of particular interest because of its feasibility for preparing large areas and mass production of devices, although the polymer rubbed alignment of FLCs creates a high polar surface anchoring effect at the boundary and gives the zig-zag defects which affect the contrast of the device.

The surface anchoring effect due to the charge accumulation phenomenon has been studied by many groups [2, 4, 5] using electro-optical methods. However, this phenomenon has been very rarely studied by dielectric relaxation methods because the mobility of the charges is very slow and hence this effect can be detected only at very low frequencies of the dielectric spectrum. The conductivity effect for lower frequencies (below 100 Hz) plays a dominant role and it increases tremendously on decreasing the frequency ($\sigma \sim \omega^{-1}$).

In the present investigations, FLC samples possessing a smectic C* (SmC*) to chiral nematic (N*) first order phase transition have been used. Optically well aligned samples were prepared by coating the polymer on one of the electrodes and rubbing. The dielectric investigations were made on such samples in the frequency range 0.01 Hz to 12 MHz for different temperatures and biasing voltages for the smectic C* and chiral nematic phases and the isotropic phase as well. The charge accumulation phenomenon has been clearly detected by the dielectric relaxation method in the present study, although it should be said that some hints regarding ionic charges were given earlier also by Kocot *et al.* [6] and Havriliak *et al.* [7] in relation to ferroelectric liquid crystal materials.

The low frequency dielectric spectrum will be discussed in terms of the Cole–Cole function:

$$\varepsilon^* = \varepsilon' - i\varepsilon'' = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + (i\omega\tau_0)^{1-\alpha}} - i\frac{\sigma}{\omega\varepsilon_s} \qquad (1)$$

where ω is the angular frequency, τ_0 is the most probable relaxation time, α is the so-called distribution parameter, ε' and ε'' are, respectively, the real (dielectric permittivity) and imaginary (dielectric loss) parts of the ε^* complex dielectric permittivity, ε_0 and ε_∞ are the low and high

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*Author for correspondence. Permanent addresses: Display Devices Group, National Physical Laboratory, K. S. Krishnan Road, New Delhi-110 012, India; e-mail: abiradar@csnpl.ren.in

†Present address: M. Smoluchowski Institute of Physics, Jagellonian University, Reymonta 4, 30-059 Krakow, Poland.

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frequency limits of the electric permittivity, ε_s is the electric permittivity of free-space and σ is the conductivity. The relaxation time τ_0 is connected with the critical frequency ν_c at which ε'' reaches its maximum, according to the equation $\tau_0 = (2\pi\nu_c)^{-1}$. $\alpha = 0$ corresponds to a single relaxation process observed for polar liquids, plastic crystalline phases and homeotropically aligned liquid crystalline phases. $\alpha > 0$ is usually observed for polymers, where many dipole moments bound to flexible molecules contribute to the dielectic relaxation process, for planar aligned liquid crystals and also for some reorientationally disordered solid phases. The α parameter describes a symmetric distribution of the relaxation times around the most probable value τ_0.

2. Experimental

Highly conducting indium tin oxide (ITO) with a sheet resistance of 20 Ω/□ coated on optically flat glass substrates was used for the electrodes which allow one to control the optical alignment of the liquid crystal molecules, as well as to study the dielectric relaxation processes in a wide frequency range. One of the electrodes was treated with adhesion promoter and polymer (nylon 6/6) and was unidirectionally rubbed. The charge accumulation effect was obtained with thick polymer coatings [8] and a strong rubbing strength which was obtained by keeping the minimum distance between the glass substrates and the rubbing block which was wrapped in a velvet cloth. Thicknesses of samples were maintained around 2.5 μm by means of photoresist film spacers. The cells were first calibrated using air and toluene as standard references. A single component FLC material was used in this investigation, 3-octyloxy-6-[2-fluoro-4-(2-fluoroctyloxy)phenyl]pyridine (in short FFP), supplied by E. Merck (Darmstadt) it has the phase sequence:

$$\mathrm{Cr}\ \underset{30^{\circ}\mathrm{C}}{\overset{43.2^{\circ}\mathrm{C}}{\longleftrightarrow}}\ \mathrm{SmC}^*\ \overset{45^{\circ}\mathrm{C}}{\longleftrightarrow}\ \mathrm{N}^*\ \overset{61^{\circ}\mathrm{C}}{\longleftrightarrow}\ \mathrm{I}.$$

The phase sequence of this material was obtained by using optical polarizing microscopy for a sample contained in the thin cell mentioned above. It differs slightly from the data published in [9]. The difference comes from the more pronounced surface effects in thin cells.

The material was introduced into the cell by means of capillary action at a temperature slightly above the N*–I transition. A well aligned sample is obtained by applying an a.c. electric field just below the N*–SmC* transition temperature and simultaneously observing the sample under the polarizing microscope. The detailed procedure for obtaining planar alignment in such types of ferroelectric liquid crystal materials is given in [10].

The dielectric measurements were made in the frequency range 0.01 Hz to 12 MHz. Two types of measuring set-up were used: (1) involving an impedance analyser (HP 4192A) in the frequency range between 10 Hz and 13 MHz and (2) using a Schlumberger Solatron-1250 frequency response analyser connected with a home-made, so-called Chelsea-type Dielectric Interface in the frequency range from 10 mHz to 30 kHz. The dielectric measurements were made under computer control and were fully automated. The relative temperature was measured with an accuracy of ± 0.01 K and was stabilized during the dielectric measurements. The dielectric measurements on the SmC* phase were made on cooling. The data were corrected for the static conductivity and for the high frequency deviations caused by the inductance and resistance of the cables and connectors. Temperature, frequency and bias field (generated by the impedance analyser) dependences of the real and imaginary parts of the complex electric permittivity were studied for the smectic C* and chiral nematic phases for planar alignment, and for the isotropic phase as well. The optical alignment was obtained by applying an a.c. electric field to the FLC cells mounted on the stage of the polarizing microscope (Leitz Wetzlar) and simultaneously dielectric measurements were taken for all the phases.

3. Results and discussions

In this study we discuss the dielectric investigations made on a single component ferroelectric liquid crystal material which shows a first order phase transition from smectic C* to chiral nematic phase. To study the charge accumulation phenomenon, a highly anchored surface was prepared with the use of an a.c. electric field [11]. In the planar alignment the measuring electric field is perpendicular to the director.

Figure 1 shows the electric permittivity as a function of temperature obtained at low frequencies. The electric permittivity is very high in the smectic C* phase, falls at the SmC*–N* phase transition and then becomes practically constant at higher temperatures in the chiral nematic phase. It is well known that with a planar alignment the electric permittivity is due to the collective dielectric processes such as the Goldstone mode, which arises from phase fluctuations, and the soft mode due to the amplitude fluctuation in the tilt angle of the molecules. The Goldstone mode is dominant over the whole SmC* phase for lower frequencies (figure 1 (*a*)), whereas the soft mode appears at higher frequencies (around 100 kHz) near the SmC*–N* phase transition temperature, figure 1 (*b*). Detailed studies of the collective dielectric processes such as the Goldstone mode, soft mode and domain mode [12] in SmC* and N* phases of this material, aligned by a magnetic field in a gold coated cell, have been reported by us elsewhere [9].

Figure 2 shows the electric permittivity data as a function of frequency acquired at different temperatures.

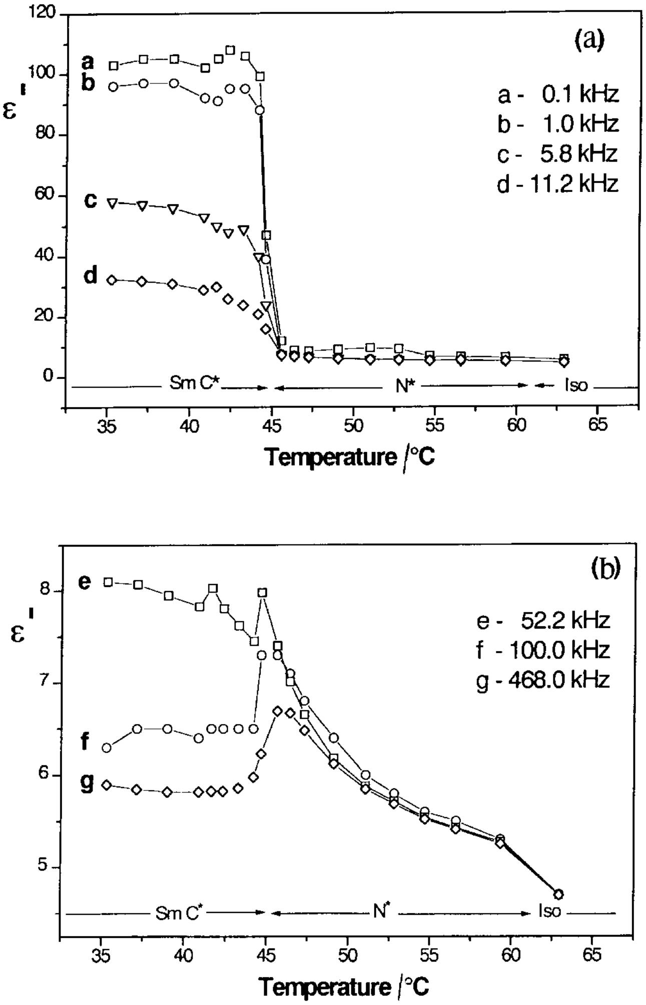

Figure 1. Temperature dependences of dielectric permittivity (ε') at different frequencies, (*a*) for lower frequency and (*b*) for higher frequency ranges.

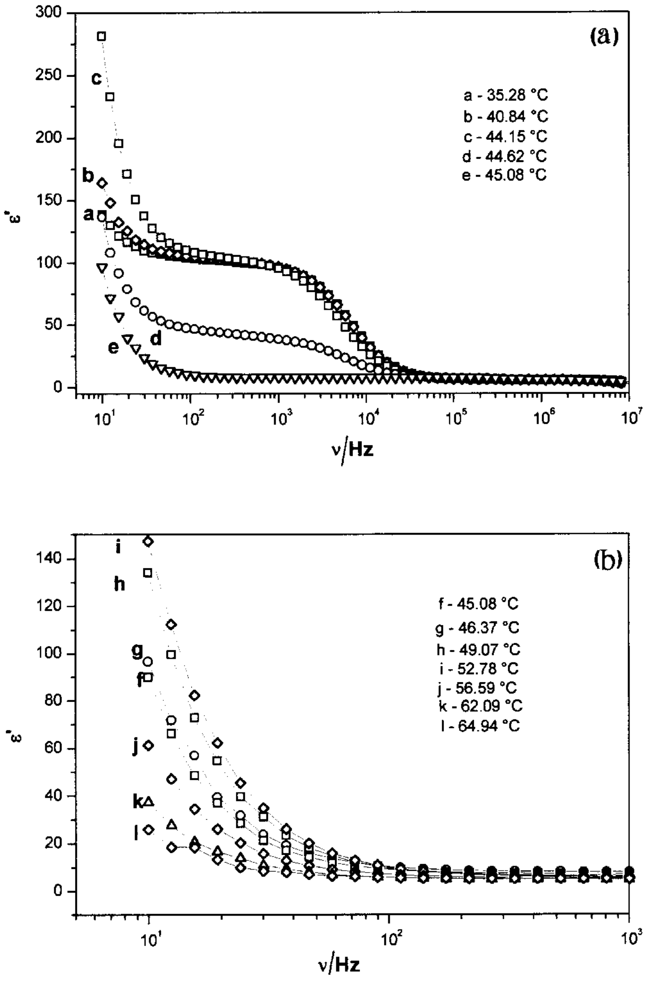

Figure 2. The behaviour of the dielectric permittivity (ε') as a function of frequency at different temperatures, (*a*) in the smectic C* and (*b*) in the chiral nematic and isotropic phases.

As one can notice, these dispersion curves can be analysed in terms of three contributions. The first contribution (which is almost constant) in evidence above 100 kHz comes from a fast molecular process exhibiting dispersion at microwave frequencies [13]. The second, occurring below 10 kHz where the electric permittivity (ε') is very high and decreases with temperature in the smectic C* phase, is the Goldstone mode contribution. The third contribution to the dielectric permittivity is below 100 Hz frequency and its intensity is temperature dependent, figure 2(*a*). This means that there is a dielectric relaxation process which is very slow and could be due either to the unwinding mode [14] or a surface effect due to the charge accumulated on the surface of the cell. This process is very clearly seen even at high temperatures in the chiral nematic phase and in the isotropic phase, figure 2(*b*).

The dielectric spectrum of the sub-hertz frequency process can be better seen by plotting the loss-factor (tan δ) as a function of frequency at different temperatures in the SmC* phase (below 45°C) as seen in figure 3. The Goldstone mode is seen in the SmC* phase and as the temperature increases it becomes weak, curves d and e of figure 2(*a*). It is interesting to see that there is a dielectric process around 10 Hz which is seen at higher temperatures in the smectic C* phase (curves c and d in figure 3). It should be pointed out here that the electric permittivity (ε') for lower frequencies (below 100 Hz) is not consistent with temperature, particularly near the transition temperature from SmC*–N* phase (45°C); this could be because the corrections for the static conductivity effect with temperature are not made in the dielectric measurements carried out by the HP 4192A impedance analyser, figure 2(*a*). However,

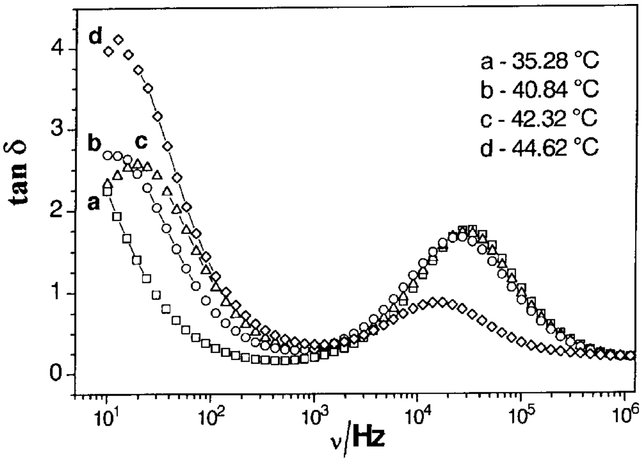

Figure 3. Loss-factor (tan δ) as a function of frequency at different temperatures in the smectic C* phase.

the low frequency dielectric measurements, made by the Solatron-1250 analyser, are consistent with temperature (figure 4) and here the corrections for the static conductivity effect with temperature have been done. In the further discussions we shall concentrate on this very low frequency dielectric relaxation process which appears as a result of a thick polymer film on one of the cell electrodes for the alignment of the ferroelectric liquid crystal molecules.

The sub-hertz frequency dielectric process could not be seen very clearly, particularly for lower temperatures in the SmC* phase, as this process appears below 10 Hz frequency. Therefore, low frequency measurements in the range 0.01 Hz to 10 kHz were conducted using the Schlumberger Solatron, 1250 frequency response analyser, where the conductivity part of the FLC material is taken into account. Figure 4 (*a*) shows the loss-factor (tan δ) versus frequency at different temperatures for the sub-hertz frequency process. It is clear that the relaxation frequency of the sub-hertz process in the SmC* phase appears below 10 Hz frequency. The relaxation frequency of this process is weakly temperature dependent. Figure 4 (*b*) shows the absorption curves (ε'' vs frequency) at different temperatures. As seen in the figure, the absorption (ε'') for lower frequencies and at higher temperatures goes up to 7000. The high value of the absorption is not surprising and is understandable because the conductivity effect at higher temperatures is enhanced [15] for lower frequencies. The same effect was observed before for some mixtures of metallomesogenes [16]. This is one reason why sub-hertz frequency dielectric measurements are difficult and rarely reported. However, in the present investigations, a low frequency dielectric process is very clearly seen even in the absorption spectra (figure 4 (*b*)) and this is mainly because of the use of the sub-hertz Schlumberger Solatron-1250 set-up. Figure 4 (*c*) shows a Cole–Cole representation of the low frequency dielectric spectrum. By fitting equation (1) to the experimental spectra, one can see that the spectrum

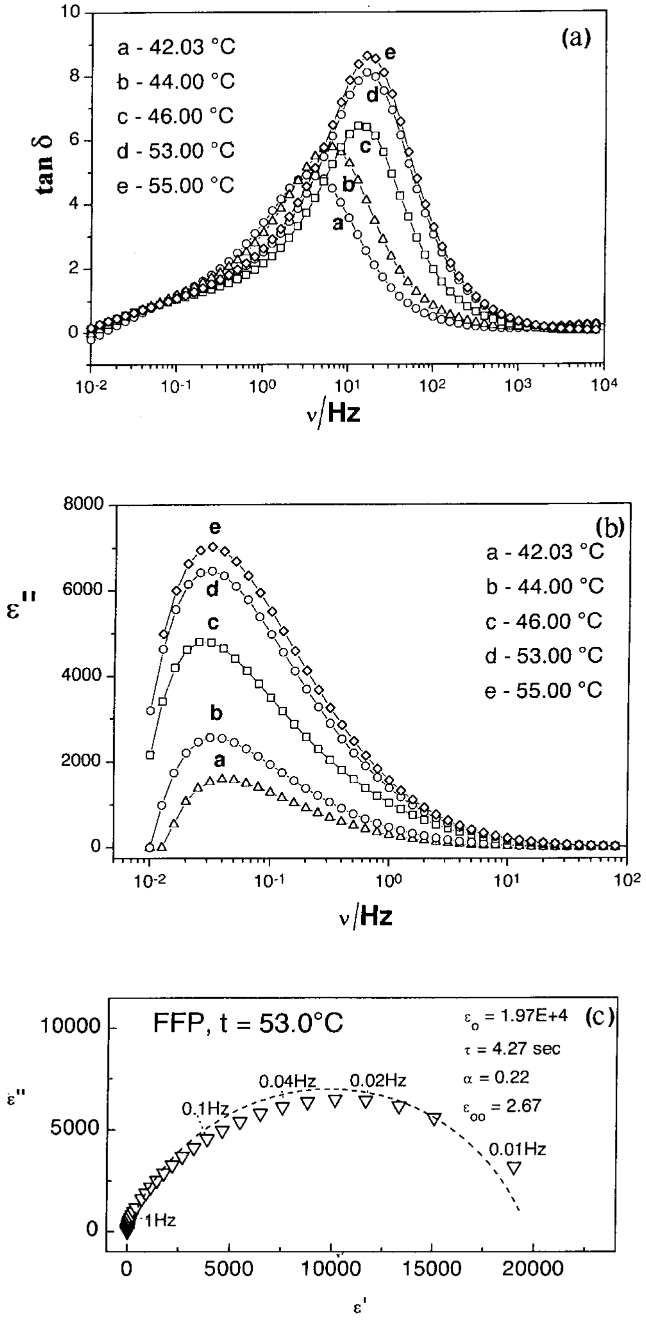

Figure 4. (*a*) Loss-factor versus frequency and (*b*) the absorption curves (ε'' vs. frequency) for very low frequencies (0.01 Hz–10 kHz) at different temperatures in the smectic C* and chiral nematic phases. (*c*) Cole–Cole representation of the sub-hertz frequency dielectric spectrum of FFP taken in the N* phase; dashed line is a fit of equation (1) to the experimental points.

observed in the sub-hertz range shows a pronounced distribution of the relaxation times. The dashed line represents a theoretical fit to equation (1) and the fitting parameters are given in figure 4 (*c*).

It is known that the maximum of $\tan\delta$ shows up at frequencies higher by a factor of $(\varepsilon_0/\varepsilon_\infty)^{1/2}$ than the respective maximum for the ε'' dielectric losses. In other words the relaxation frequencies for the $\tan\delta$ dielectric spectrum $[\nu_R(\tan\delta)]$ and the ε'' dielectric spectrum $[\nu_R(\varepsilon'')]$ are connected by the formula [17]:

$$\nu_R(\tan\delta)=\nu_R(\varepsilon'')(\varepsilon_0/\varepsilon_\infty)^{1/2}. \qquad (2)$$

Due to this relation for highly polar dielectrics, the low frequency absorption peaks observed for $\tan\delta(\nu)$ may not be observed for $\varepsilon''(\nu)$ as they become shifted to very low frequencies, as seen in figures 4 (*a*) and 4 (*b*). Another point to be noted in the loss-factor and imaginary part of the spectrum is that the relaxation frequency is weakly temperature dependent in the loss-factor (figure 4 (*a*)), whereas in the imaginary spectrum it is independent of temperature (figure 4 (*b*)). This discrepancy could be due to the fact that the dielectric permittivity (ε') in the sub-hertz region is very high, even going up to 15 000, and when ε' is multiplied by the loss-factor to calculate the imaginary part (ε''), the weak dependence of the relaxation frequency on temperature is not reflected in the absorption spectrum, figure 4 (*b*).

The effect of bias field on this very low frequency dielectric process was studied by using the internal bias of the impedance analyser (HP 4192A). The bias field dependences were studied at higher temperatures because this process appears clearly at higher temperatures and also above 10 Hz frequency. Figure 5 (*a*) shows the behaviour of the electric permittivity for different bias voltages. As seen in the figure, at high bias voltage (5 V) this process is almost suppressed. It is surprising to see here that this slow process is very strong and needs very high fields of the order of ~ 5 V/2.5 μm to be suppressed. The behaviour of the loss-factor ($\tan\delta$) at different bias voltages is similar, as shown in figure 5 (*b*).

The sub-hertz dielectric relaxation process in the present investigation cannot be due to the unwinding mode predicted by Zeks *et al.* [14] because this process appears at zero bias field. Further, they argue that the unwinding mode is associated with the Goldstone mode, but in the present study the low frequency process is observed even in the chiral nematic and isotropic phases. The other possibility could be the presence of ionic impurities in the FLC material, but this can also be ruled out because this low frequency dielectric process could not be detected when the material is aligned by a magnetic field [9]. Moreover, the investigated FLC material is single component and seems to be very stable.

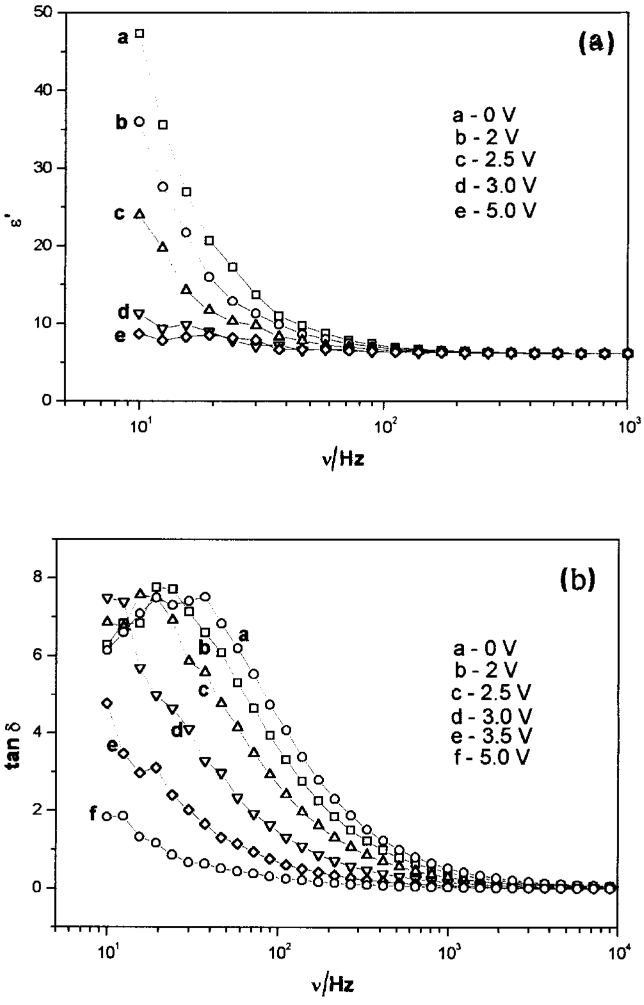

Figure 5. Effects of biasing voltages on the very low frequency dielectric process at 56.04°C; (*a*) Figure gives ε' vs. frequency and (*b*) $\tan\delta$ vs. frequency.

It is known [8, 9] that in surface stabilized ferroelectric liquid crystal (SSFLC) cells, the surface bistability is lost, mostly due to the accumulation of free charges at the interface between the FLC medium and the insulating alignment layers; this depends on the nature of the alignment layers and is found to be very high for nylon 6/6 polymer [2]. It is also known that the use of high spontaneous polarization FLC materials improves the switching speed, but destroys the bistability due to charge accumulation. To study the charge accumulation phenomenon by the dielectric relaxation method, a high spontaneous polarization FLC material (160 nC cm^{-2}) and a thick coating of polymer of 1000 Å for the alignment were used. The dielectric relaxation method clearly detects the charge accumulation phenomenon at very low frequencies which is understandable because the mobility of the charges is very low. From figures 2 (*a*) and 2 (*b*), it is clear that this dielectric process appears in the SmC* and N* phases and also a few degrees into the isotropic phase, suggesting that the low frequency process is not due to the FLC material characteristics, but to the charge accumulation in the surface layers. Of course, the charge accumulation is enhanced by the high $\mathbf{P}_s$ value of the FLC material. It is worth mentioning here that in electro-optical studies, the charge accumulation phenomenon, which results in asymmetric switching [10, 18] of the liquid crystal molecules, is very clearly observed with high tilt angle materials aligned by coating one surface of the cell by rubbed polymer.

It should be stressed here that the sub-hertz dielectric process could not be detected in this FLC material when the polymer layer for the alignment was thin. The charge accumulation is favoured by high spontaneous polarization material and one may then argue about why this process is seen in the cholestric phase where there is no local spontaneous polarization. This is because smectic-like ordering is retained in the polymer rubbed surface layers, resulting in the appearance of the sub-hertz dielectric process in the cholestric phase and even in the isotropic phase, curves j and k in figure 2 (*b*). Smectic-like ordering has also been observed in cholestric and isotropic phases due to surface effects and results in the appearance of the electro-clinic effect in these phases [19, 20]. It is worth mentioning that this sub-hertz dielectric process could not be seen in low $\mathbf{P}_s$ value material [21], suggesting that the charge accumulation phenomenon is favoured by high spontaneous polarization FLC material and a thick polymer coating for the alignment.

The sub-hertz frequency dielectric process is dependent on the bias field (figure 5), suggesting that the charges accumulated between the insulating alignment layer and the ferroelectric liquid crystal material can be annulled by the bias field. Evidence of such annulling of the effect of the accumulated charges by applying a bias field has also been observed in electro-optical studies [22] of the first order phase transition in a high tilt angle FLC material.

The sub-hertz dielectric process must indeed be due to the charge accumulation phenomenon in the surface layers, because under the same experimental conditions of cell preparation with such types of FLC materials, the charge accumulation in the surface layers has been observed by electro-optical methods [11, 18, 20, 22]. The difference in the present investigation is that we were able to establish very clearly the relaxation frequency (time) of the charges accumulated in the surface layers by the dielectric method in the sub-hertz frequency range.

4. Conclusions

(1) The dielectric relaxation method reveals the charge accumulation phenomenon between the alignment layer and the ferroelectric liquid crystal material at sub-hertz frequencies.
(2) The sub-hertz dielectric relaxation process due to the charge accumulation phenomenon is observed in the smectic C* phase, the chiral nematic phase and a few degrees into the isotropic phase in this material showing a first order SmC*–N* phase transition.
(3) The charge accumulated in the surface layers can be annulled by applying an external bias field.

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