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Preliminary communication

Low frequency dielectric relaxation in the smectic C* phase of a ferroelectric liquid crystal

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Dielectric measurements were made on the ferroelectric liquid crystal Felix® 018/100 manufactured by Hoechst, Germany, over the temperature range 30 to 65°C (smectic C* phase), frequency range 0.1 Hz to 100 kHz, with bias voltages of 0, 1, 3 and 10 V, and in a dielectric cell with a spacing of 4 times the helical pitch. Plots of the dielectric loss versus log (frequency) show the usual monotonic increase in the loss with decreasing frequency, as well as the usual loss peak at approximately 1 kHz. Plots of the log (dielectric loss) against log (frequency) at low frequencies, have slopes varying from -0.75 to -0.89 when the temperature increases from 30 to 65°C. Following the suggestion of Scaife, transforming the complex permittivity data to the complex polarizability of a sphere of unit radius in a vacuum, and plotting the loss polarizability against log (frequency), shows two distinct and separate loss peaks. The sums of the two loss peaks appear to be independent of temperature and bias voltage, even though both depend on these variables.

Dielectric measurements on ferroelectric liquid crystals (FLCs) are generally discussed in terms of the complex relative permittivity, $\varepsilon(\omega)$, (assumption I), defined as

$$\varepsilon(\omega) = \varepsilon'(\omega) - \mathrm{i}\varepsilon''(\omega) \tag{1}$$

where $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ denote the real and imaginary parts of the relative permittivity. Assumptions underlying the use of $\varepsilon(\omega)$ as applied to intermolecular processes have been discussed in some detail [1–3]. In the work cited, the complex polarizability, $\rho(\omega)$, of a sphere of unit radius suspended in vacuum is recommended for analysis. This quantity is related to $\varepsilon(\omega)$ through

$$\rho(\omega) = \rho'(\omega) - \mathrm{i}\rho''(\omega) = \frac{\varepsilon(\omega) - 1}{\varepsilon(\omega) + 2}. \tag{2}$$

Dielectric relaxation measurements are made as as a function of frequency $f = \omega/2\pi$, at constant temperature, and carried out for different bias voltages. ω is the frequency in rad s^{-1}. The temperature is then altered and the entire process repeated. At low frequencies, $f < 10$ Hz, plots of $\varepsilon''(\omega)$ with log (frequency) reveal a monotonic increase of the loss with decreasing frequency. This behaviour is often described as a 'd.c. tail' implying that the migration of charged impurities through the system is its origin (assumption II).

If the low frequency behaviour can be represented by ionic impurities in a fluid such as an ionic salt dissolved in a polar solvent, then the conductance G, calculated from the loss permittivity, i.e. equation (3)

$$\varepsilon''(\omega) = \frac{G}{\omega C_0} \tag{3}$$

should be independent of frequency; C_0 is the geometrical capacitance of the cell. For ionic crystals, one might expect a 'hopping' or jumping process to model this behaviour. In this case the representation might have Debye-like character. An examination of assumptions I and II above is the object of this work.

The FLC mixture, Felix® 018/100, is manufactured by Hoechst‡. The smectic C* phase exists over the temperature range -9 to 67°C, and the helical pitch is 25 μm. Sample cells for dielectric measurements consisted of indium tin oxide (ITO) coated glass plates with a resistance of $< 30\,\Omega/\square$. For planar homogeneous alignment, the conducting inner surfaces were spin coated with a polyvinyl alcohol (PVA) alignment layer and rubbed parallel to the surface after drying. The glass plates were separated by 100 μm Mylar spacers to form

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a dielectric cell. The cells were filled in the isotropic phase, i.e. > 90°C. Textures of the experimental cells were observed using a polarizing microscope. Dielectric measurements in the frequency range 0.1 Hz to 100 kHz were made using a Schlumberger 1225A frequency response analyser with a Chelsea dielectric interface. Temperatures used for the measurements ranged from 30 to 65°C, incremented by 5°C. Frequency sweeps were made at bias voltages of 0, 1, 3 and 10 V at each of the temperatures.

In figure 1, we plot $\varepsilon''(\omega)$ as a function of $\log(f)$ for a number of temperatures and a bias voltage of 1.0 V. This plot is similar to those reported elsewhere, [4], except that our frequencies were extended down to 0.1 Hz. There is a loss maximum in the 10 kHz region attributed to the Goldstone mode. At lower frequencies, the loss appears to increase seemingly without an upper limit. Slopes determined from $\log[\varepsilon''(\omega)]$ vs. $\log(f)$ plots in this low frequency range varied systematically from 0.35 at 30°C to 0.89 at 65°C. Plots of $\log(G)$ vs. $\log(f)$ are given in figure 2 for the same temperatures, but the frequency range is below 5 Hz. Slopes determined from these $\log(G)$ vs. $\log(f)$ plots are also temperature dependent and varied from 0.35 at 30°C to 0.06 at 65°C.

In figure 3 the imaginary part of the polarizability, $\rho''(\omega)$ is plotted as a function of log (frequency) for different temperatures and a bias voltage of 1.0 V. Over the entire temperature range, two $\rho''(\omega)$ peaks are observed. Furthermore as the temperature increases, the magnitude of the high frequency loss peak decreases, while the magnitude of the low frequency process increases by about the same amount. This also leads to the observation that the sum of the two loss peaks at any temperature is approximately the same. Furthermore the frequency of the Goldstone peak remains almost independent of temperature, while the frequency of the low frequency $\rho''(\omega)$ peak increases with increasing temperature.

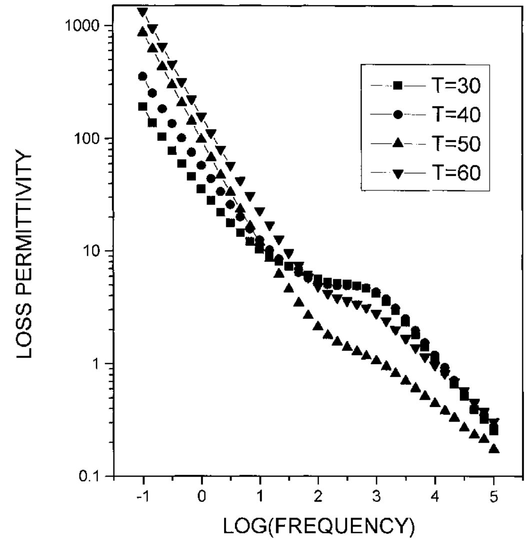

Figure 1. Plot of $\varepsilon''(\omega)$ of the loss permittivity as a function of log (frequency) for the temperatures listed and a bias voltage of 1.0 V.

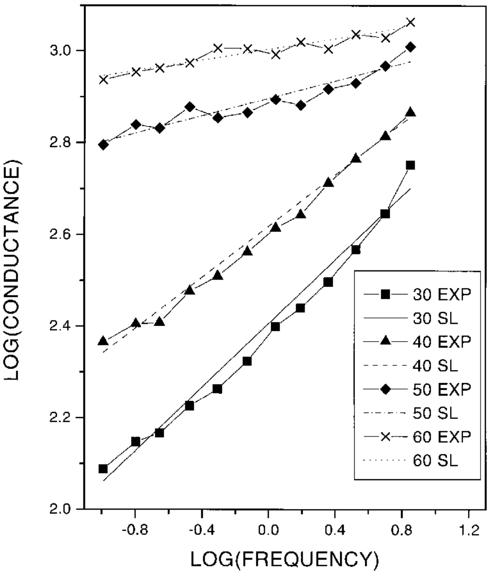

Figure 2. Plot of $\log(G)$ as a function of $\log(f)$ under the same conditions as those in figure 1 but limited to a frequency < 5 Hz. EXP in the inset means experimental while SL means straight line fit.

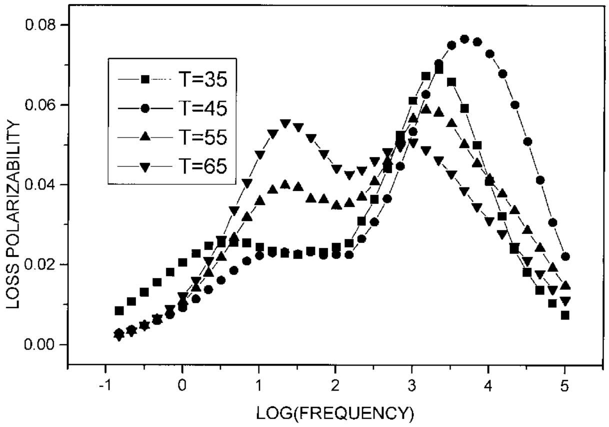

Figure 3. Plot of the loss polarizability as a function of log (frequency) for the temperatures listed in the inset and a bias voltage of 1.0 V.

In figure 4 we plot $\rho''(\omega)$ as a function of $\log(f)$ for a series of bias voltages and $T = 50$°C. This figure also shows two maxima in $\rho''(\omega)$. The high frequency $\rho''(\omega)$ peak decreases with increasing voltage, while the low frequency peak has the opposite dependence. The sum of the two peak heights at constant bias voltage appears to be independent of the bias voltage. The two $\rho''(\omega)$ peaks can be represented as the sum of two H–N

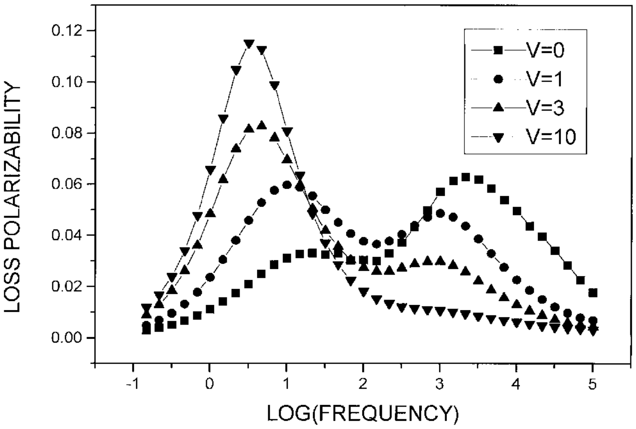

Figure 4. Plot of the loss polarizability as a function of log (frequency) for the bias voltages listed in the inset and at 50°C.

functions [5], i.e.

$$\rho(\omega) = \rho_{\infty} + \sum_{i} \frac{\Delta \rho_i}{[1 + (\mathrm{i}\omega \tau_{0i})^{\alpha_i}]^{\beta_i}}. \tag{4}$$

Estimation of the H–N parameters is straightforward [6, 7], and these along with their confidence intervals are given in the table for the bias voltage of 1.0 V and $T = 50$°C.

Scaife's suggestion leads to the remarkable result reported in this work, i.e. that a 'DC tail' plus a loss peak in the $\varepsilon(\omega)$ representation is transformed into two loss peaks in the $\rho(\omega)$ representation of the dielectric dispersion data. Scaife's polarizability plot is based on an analysis using fluctuation theory. Although the plot is more successful in revealing the high frequency processes than the Cole–Cole plot, the usefulness of the plot at low frequencies has not been shown before. We have cited a number of the interesting results in the introductory part of this work.

Table. Dispersion parameters at 50°C and a bias voltage of 1.0 V. Model standard error of estimate = 0.7%.

	High frequency process		Low frequency process	
Parameter	Value	σ_1 [a]	Value	σ_2 [b]
Δp_i	0.114	0.002	0.179	0.002
$\ln f_0$ [c]	6.71	0.02	1.40	0.03
α	0.95	0.01	0.815	0.005
β	0.53	0.01	0.55	0.02

[a] σ_1 = confidence interval (standard deviation) in the polarizability increment (static polarizability – infinite frequency polarizability) of the low frequency process.

[b] σ_2 = confidence interval (standard deviation) in the polarizability increment of high frequency process.

[c] $f_0 = 1/(2\pi\tau_0)$ where τ_0 is the relaxation time of the corresponding process.

Δp_i is the polarizability increment for the i-th process.

There are probably two reasons why the dielectric relaxation data are usually discussed in terms of $\varepsilon(\omega)$, (assumption I). First, it is an experimentally measured quantity; second, the pioneering work of Onsager [8], Kirkwood [9], and Cole [10] has shown that $\varepsilon(\omega)$ is related to the molecular quantities under the specific conditions of polar liquids that can be represented as point dipoles. The macroscopic model chosen for their purposes is a sphere of the specimen suspended in vacuum, as mentioned earlier. Eventually the sphere is divided into two concentric spheres, a microsphere containing all the elements of local structure represented by point dipoles and a macrosphere represented by a continuum. In this idealized model, the long range correlations between molecules are replaced by an electrostatic interactions between the dipole(s) in the microsphere within the macrosphere.

If we consider, the original macrosphere to consist of a helicoidal structure of FLC, then the major problem is 'What is the size of the microsphere chosen to represent the local structure?' The microsphere may very well be the same size as the macrosphere due to the helicoidal structure of the liquid crystal, which is rather isotropic.

The behaviour of $\varepsilon''(\omega)$ with $\log(f)$ at low frequencies is not consistent with any simple interpretation in terms of ionic impurities. Transformation of $\varepsilon(\omega)$ to $\rho(\omega)$ reveals another loss peak with dispersion characteristics similar to many polar materials, including polar liquids, as well as polymers. In addition, an Arrhenius rate plot of the loss maximum frequency with temperature for the low frequency process is about 7 kcal mol^{-1}. The origin of this process is uncertain and future work is underway to define its nature.

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