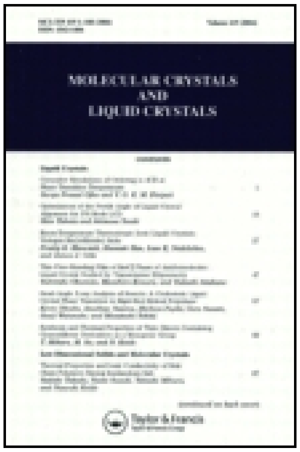

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Complex Dielectric Constant of Liquid Crystal Materials Containing Ionic Impurities in Low Frequency Region

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Complex Dielectric Constant of Liquid Crystal Materials Containing Ionic Impurities in Low Frequency Region

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The dielectric properties of liquid crystal materials containing ionic impurities are analyzed in terms of space charge polarization. The theoretical expressions of the dielectric constant and the dielectric loss factor are derived by solving a diffusion equation for mobile ions under an AC field. Numerical calculations are performed using the theoretical expressions and the frequency dependent dielectric behaviors are simulated. The calculated curves for the dielectric constant and the dielectric loss factor exhibit a dielectric dispersion and a dielectric absorption respectively in a low frequency region, and successfully trace the observed curves obtained for liquid crystal materials 4-n-pentyl-4'-cyanobiphenyl (5CB) by means of curve fitting with the parameters of the diffusion coefficient and the density of mobile ions.

Keywords: mobile ions; dielectric constant; dielectric loss factor; diffusion coefficient

INTRODUCTION

It is known that dielectrics containing ionic impurities exhibit an anomalous increase in the complex dielectric constant in a low frequency region and a dielectric relaxation appears in a lower frequency region, which is characteristic to the behavior of the ions. Similar phenomena can also be observed in liquid crystal materials as well.[1]-[3] In case of liquid crystal materials, mobile ions are considered to cause deteriorations of display qualities[4][5], and so it is significantly important to investigate the complex dielectric constant of liquid crystal materials, in which the behavior of mobile ions is clearly reflected. The increase in the complex dielectric constant in a low frequency region is considered to be due to polarizations at electrodes, namely due to the space charge polarization. Macdonald[6] and Friauf[7] theoretically analyzed the space charge polarization considering charge mobilities, but the relations between space charge effects and charge mobilities are fairly complicated and the obtained results are not necessarily expressed in such a form as we intend to use for comparison with our experimental results.

For polymer materials containing ionic impurities, Uemura[8][9] simplified the space charge effects and derived the theoretical expression for the complex dielectric constant solving a diffusion equation for mobile ions under an AC field with DC bias. He applies a kind of perturbation theory in order to solve the equation providing that the AC field is weak enough in comparison with the DC field. Although Uemura's expression is explained to be applicable to the case in the absence of DC bias, as there is no DC field in our case, his assumption is no longer valid for our case in a mathematical sense.

We perform a different kind of perturbation theory in this paper, to find out whether Uemura's equations can also be applicable to our case without DC bias. Uemura compared his theory with experimental results for polymers assuming that the diffusion distance in a period of the external field should be smaller than the thickness of the specimen. In this case, it is reported that the expression is valid in an appropriate frequency range where the condition is hold and can represent the increasing behavior of the dielectric constant or the dielectric loss factor, but a dielectric relaxation which will appear in a lower frequency region can not be represented by the expression. For cases where the condition of the diffusion distance is not fulfilled, we performed numerical calculation of the frequency dependence of the complex dielectric constant, and found that the dielectric relaxation appears in the low frequency region and that the peak frequency for the dielectric loss factor becomes higher with decreasing the thickness of the specimen.

In this paper, the simulation results on the frequency dependence of the complex dielectric constant will be shown and the results will be compared with observed values for the liquid crystal material 5CB.

THEORETICAL ANALYSIS OF COMPLEX DIELECTRIC CONSTANT

The system under consideration is assumed to be treated by one dimensional diffusion equation,

$$\frac{\partial f}{\partial t}=-\frac{\partial J}{\partial x} \tag{1}$$

with

$J(x,t)$: flux of ion at the point of x and time t

$f(x,t)$: distribution function of the ion density

The flux J can be described to have the form,

$$J = -D\frac{\partial f}{\partial x} + \frac{qF_o}{\varsigma}e^{i\omega_o t}f \quad . \tag{2}$$

The first term stands for the diffusion with diffusion coefficient D. The ionic impurities are assumed to be under the influence of the local alternating field with a frequency ω_o. Taking the friction term (friction coefficient ς) into consideration and noticing that the ionic particle reaches the velocity, given as the ratio between the alternating force and the friction force, in a very short scale compared with the time scale under consideration, the additional flux term can be described as the second term (q :the charge of an ion, F_o :the amplitude of the local alternating field acting on ions, $i = \sqrt{-1}$).

Altogether the diffusion equation is

$$\frac{\partial f}{\partial t} = D\frac{\partial^2 f}{\partial x^2} - \frac{qF_o e^{i\omega_o t}}{\varsigma}\frac{\partial f}{\partial x} \quad . \tag{3}$$

As a boundary condition of this diffusion equation no flux condition is applied for the sake of simplicity, namely

$$J\Big|_{boundary} = 0 \quad . \tag{4}$$

The diffusion equation (3) has an explicit time dependence in the second term of the right hand side. Therefore, it is difficult to find a general expression of the solution without any assumption. We are now interested in the behavior of the ionic impurities in the low frequency region. Physically speaking we should study the slowly varying behavior of the ionic impurities in time. We take a mathematical advantage of it assuming the following perturbation,

$$f = f_0(x) + F_0 e^{i\omega_0 t} f_1(x,t) + O(e^{2i\omega_0 t}) f_2(x_1,t) \tag{5}$$

where,

f_o : the most slowly time varying term, namely steady state solution

$F_o\, e^{i\omega_o t} f_1$: the next slowly time varying term as the frequency of ω_o

$O\left(e^{2i\omega_o t}\right) f_2$: the further higher order term

Substituting this expansion into the diffusion equation (3), one finds as the first order,

$$\frac{\partial f_o}{\partial t} = D\frac{\partial^2 f_0}{\partial x^2} = 0 \quad , \tag{6}$$

and as the second order,

$$\frac{\partial f_1}{\partial t} + i\omega_o f_1 = D\frac{\partial^2 f_1}{\partial x^2} - \frac{q}{\varsigma}\frac{\partial f_o}{\partial x} \tag{7}$$

with the belonging boundary condition,

$$-D\frac{\partial f_1}{\partial x} + \frac{q}{\varsigma} f_o \Big|_{boundary} = 0 \quad . \tag{8}$$

The first order of the steady state solution f_o can be simply solved together with the boundary condition,

$$f_o = \frac{1}{d} \tag{9}$$

with d : the thickness of the specimen.

In order to solve the second order partial differential equation, one can assume the following solution form,

$$f_1(x,t)=e^{\lambda t}g_1(x) \quad . \tag{10}$$

Taking the boundary condition into consideration, one finds the solution as the form of

$$f_1=e^{\lambda t}\frac{q}{\varsigma d z D}\left(\frac{e^{zx}}{1+e^{zx}}-\frac{e^{-zx}}{1+e^{-zx}}\right) \tag{11}$$

with $z=\sqrt{\frac{i\omega_o}{D}}$.

All negative real values are allowed as the eigen values of λ. It means mathematically that all solutions relax with the relaxation constant of $|1/\lambda|$ to the marginal solution,

$$f_1(x,t)\,|_{\lambda=0} \quad . \tag{12}$$

The dielectric polarization P due to the displacement of ions in a unit volume is

$$P=qn\left(\bar{x}-\bar{x}_o\right) \tag{13}$$

with

n : number of ions in a unit volume

$\bar{x}$: mean average position of the ions under the AC field,

$$\int_0^d x f_1 \, dx$$

$\bar{x}_o$: mean average position of the ions without the AC field,

$$\int_0^d x f_0 \, dx \quad .$$

Thus, P can be obtained as the form of

$$P = q n F_o e^{i\omega_o t} \int_0^d x f_1 \, dx \quad . \tag{14}$$

Since the complex dielectric constant $\varepsilon_i *$ is defined as the proportional constant between P and the external electric field $E_o e^{i\omega_o t}$, then

$$\varepsilon_i * = \frac{4\pi q n F_o}{E_o} \int_0^d x f_1 \, dx \quad . \tag{15}$$

Here, we assume that the local electric field is equivalent to the external electric field. This is valid as long as the orientation of the directors of liquid crystals does not change and the amount of the ionic impurities is not so high. This is guaranteed in case of our experimental system.

Altogether the complex dielectric constant due to an ionic contribution is obtained as

$$\varepsilon_i * = \varepsilon_i ' - j\varepsilon_i '' \quad , \tag{16}$$

where

$$\varepsilon_i ' = -\left(\frac{4\pi n q^2 D}{\omega k T R} \right) \left\{ \frac{1 + 2e^R \sin(R) - e^{2R}}{1 + 2e^R \cos(R) + e^{2R}} \right\} \tag{17}$$

$$\varepsilon_i''=\left(\frac{4\pi nq^2D}{\omega kT}\right)\left[1+\frac{1-2e^R\sin(R)-e^{2R}}{R\left\{1+2e^R\cos(R)+e^{2R}\right\}}\right] \tag{18}$$

$$R=d\sqrt{\omega/2D} \tag{19}$$

, which is identical to Uemura's formula as a result.

We finally obtain Eq.(20) and Eq.(21) for the relative dielectric constant and the relative dielectric loss factor of dielectrics containing ionic impurities,

$$\varepsilon'=\varepsilon_s'+\varepsilon_i' \tag{20}$$

$$\varepsilon''=\varepsilon_s''+\varepsilon_i'' \tag{21}$$

where ε_s' is the intrinsic value of relative dielectric constant without the contribution of mobile ions, and ε_s'' is the intrinsic value of relative dielectric loss factor as well.

CALCULATED FREQUENCY DEPENDENCE OF COMPLEX DIELECTRIC CONSTANT

We carried out numerical calculations on the frequency dependence of ε' and ε'' by utilizing Eq.(20) and Eq.(21). (For the simulation we eliminated ε_s'' in Eq.(21) this time, because the value is much smaller than the value of ε_i'' in the measurement condition for 5CB used for the experiment.) It is found from Eq.(20) and Eq.(21) that the frequency dependence of the dielectric constant and the dielectric loss factor depends on the thickness, the diffusion coefficient and the density of ions. Under the condition, $\varepsilon_s'=10.9$ (we used this value in accordance with the result for 5CB measured at 1kHz,50℃), $D=1.0\times10^{-7}(cm^2/s)$, $n=1.0\times10^{15}(cm^{-3})$, we simulated the frequency dependencies of ε' and ε'' changing the thickness value.

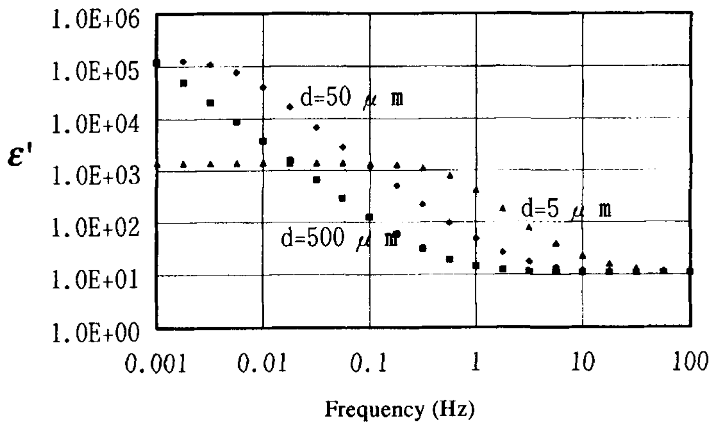

FIGURE 1 Calculated Dielectric Constant for Different Cell Thickness Values

$\varepsilon_s' = 10.9$, $D = 1.0\times10^{-7}(cm^2/s)$, $n = 1.0\times10^{15}(cm^{-3})$

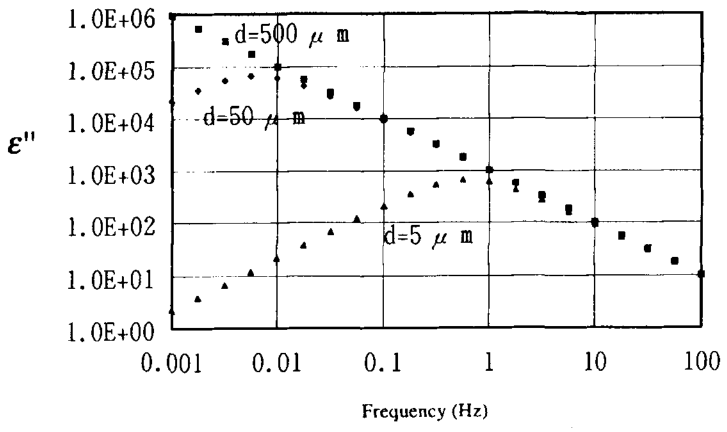

FIGURE 2 Calculated Dielectric Loss Factor for Different Cell Thickness Values

$D = 1.0\times10^{-7}(cm^2/s)$, $n = 1.0\times10^{15}(cm^{-3})$

The results are given in Fig.1 and Fig.2. The ε' for 500μm thickness monotonously increases with decreasing frequency in the range between 0.001Hz and 1Hz, but ε' for 50μm or 5μm thickness show relaxations of the increase, and the curve of ε' moves to higher frequency side and the saturated value in a low frequency range decreases with decreasing the thickness value. On the other hand, ε'' for 500μm thickness monotonously increases with decreasing frequency in the range between 0.001Hz and 100Hz, but ε'' for 50μm thickness gives a maximum value at around 0.007Hz and ε'' for 5μm thickness gives a maximum value at around 0.7Hz. The maximum value decreases with decreasing the thickness value.

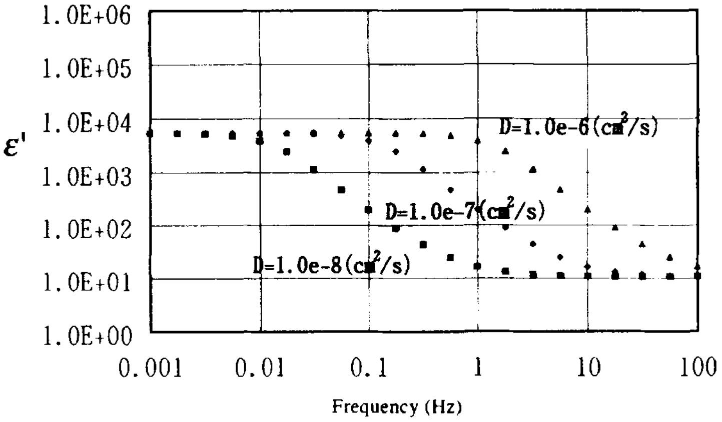

FIGURE 3 Calculated Dielectric Constant for Different Diffusion Coefficient Values
$\varepsilon_s' = 10.9$, $n = 1.0\times10^{15}(cm^{-3})$, $d = 10\mu m$

The simulated results for ε' obtained by changing the diffusion coefficient under the conditions, $\varepsilon_s' = 10.9$, $n = 1.0\times10^{15}(cm^{-3})$, $d = 10\mu m$ are given in Fig.3 and the results for ε'' as well is given in Fig.4.

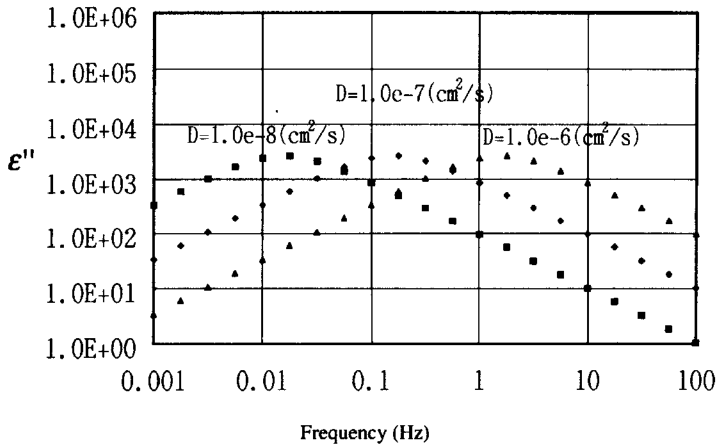

FIGURE 4 Calculated Dielectric Loss Factor for Different Diffusion Coefficient Values
$n = 1.0\times10^{15}(cm^{-3})$, $d = 10\mu m$

The curve of ε' moves to higher frequency side with increasing the diffusion coefficient but there is no change for the saturated values of ε'. The curve of ε'' moves to higher frequency side with increasing the diffusion coefficient but there is no change for the maximum value of ε''. The results for ε' obtained by changing the density under the conditions, $\varepsilon_s' = 10.9$, $D = 1.0\times10^{-7}(cm^2/s)$, $d = 10\mu m$, are given in Fig.5 and the results for ε'' as well are given in Fig.6. The relaxation frequency for ε' does not change against the increase of the density but the saturated value increases. The frequency, at which ε'' becomes a maximum value, does not change but the maximum value increases with increasing the density in the whole frequency range.

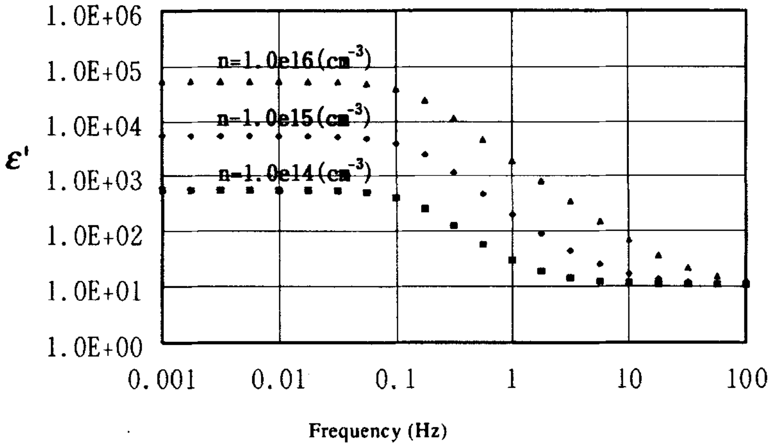

FIGURE 5 Calculated Dielectric Constant for Different Density Values
$\varepsilon_s' = 10.9$, $D = 1.0\times 10^{-7}(cm^2/s)$, $d = 10\mu m$

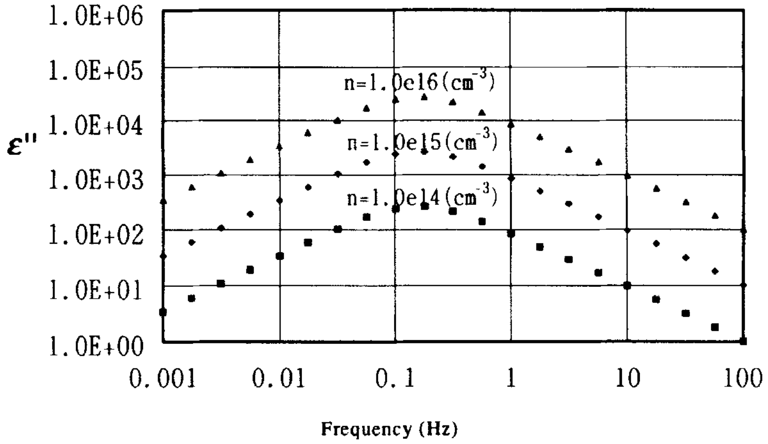

FIGURE 6 Calculated Dielectric Loss Factor for Different Density Values
$D = 1.0\times 10^{-7}(cm^2/s)$, $d = 10\mu m$

EXPERIMENTAL

We measured the frequency dependence of ε' and ε'' for a liquid crystal material 5CB applying AC 0.03V in the range between 0.1Hz and 1000Hz at 50℃ where it is in isotropic phase, utilizing the impedance measuring system Solartron 1260 with MAP software supplied from Toyo Technica. Parallel plate glass cells with ITO, the thickness 4.4μ m and 9.0μ m, were used for the measurement. The results for ε' are given in Fig.7. The dielectric relaxations are observed for both 4.4μ m and 9.0μ m cells, and as expected from the simulated results, the curve of ε' for 4.4μ m cell exists at higher frequency side than that of 9.0μ m cell and the saturated value of ε' for 4.4μ m cell becomes smaller than that of 9.0μ m cell.

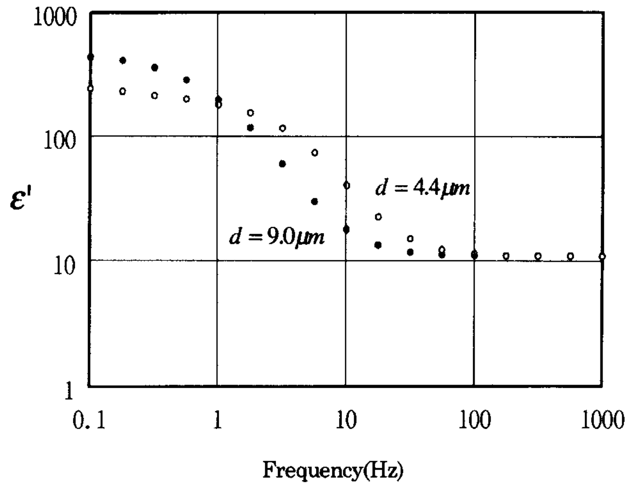

FIGURE 7 Frequency Dependence of Dielectric Constant of 5CB at 50℃

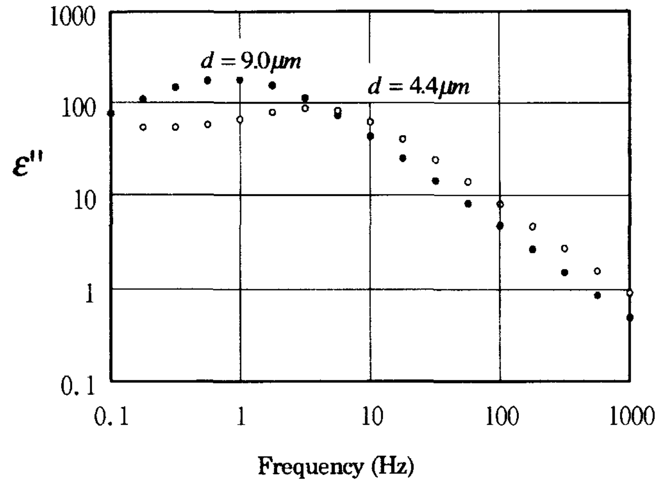

FIGURE 8 Frequency Dependence of Dielectric Loss Factor of 5CB at 50℃

The results for ε'' are given in Fig.8. The frequency giving maximum ε'' value for 4.4μ m cell exists at higher frequency than that of 9.0μ m cell and the maximum value of ε'' for 4.4μ m cell becomes smaller than that of 9.0 μ m cell.

COMPARISON WITH THEORETICAL CURVES AND DISCUSSION

We compared the experimental results with theoretical curves on the frequency dependencies of ε' and ε'' for 5CB obtained by using 9.0μ m cell. The calculated curves are derived by fitting to the experimental values changing the parameters, the diffusion coefficient D and the density n.

The results are given in Fig.9. It is found from Fig.9 that the calculated curves successfully trace the experimental results. By means of curve fitting, we obtained $4.7\times10^{-7}(cm^2/s)$ for D value and $1.0\times10^{14}(cm^{-3})$ for n value.

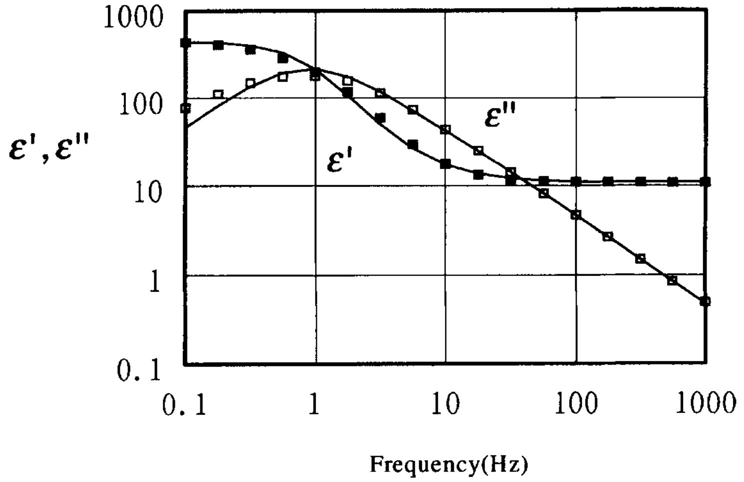

FIGURE 9 Frequency Dependence of ε' and ε'' of 5CB at 50℃
Symbols : Observed values, Lines : Calculated values

There have been many studies of transient current for 5CB in the nematic phase, and the density and the drift mobility of mobile ions are estimated to be in the order of $10^{13}(cm^{-3})$ or $10^{14}(cm^{-3})$ [10][11] and in the order of $10^{-6}(cm^2/Vs)$ [11]-[13] respectively. The obtained value $1.0\times10^{14}(cm^{-3})$ for the density is in the range of the values by transient currents studies. The drift mobility μ can be evaluated from the value of diffusion coefficient using Einstein's relation $\mu = qD / kT$. We obtained $1.7 \times 10^{-5} (cm^2 / Vs)$ for the μ value in the isotropic phase at 50℃.

For the derivation of theoretical expression of the complex dielectric constant, we assumed that the ions do not interact. It is essential to confirm whether the assumption is suitable for the condition of ions density value $1.0 \times 10^{14} (cm^{-3})$. In case the interaction among the ions is negligible, the Coulomb potential, $q^2 / 4\pi\varepsilon_o \varepsilon_r r$, should be smaller than the thermal energy, kT. We evaluated the relation utilizing following expressions in accordance with Debye-Huckel theory.

$$r_D{}^2 = \frac{\varepsilon_o \varepsilon_r RT}{2\rho N_A{}^2 q^2 I} \tag{22}$$

$$X = \left(\frac{q^2}{4\pi \varepsilon_o \varepsilon_r r_D} \right) \left(\frac{1}{kT} \right) \tag{23}$$

where r_D is the Debye length, ε_o the dielectric constant in vacuum, ε_r the relative dielectric constant of solvent, R the gas constant, ρ the density of solvent, N_A the Avogadro constant, I the ionic strength. The value of ion density, $1.0 \times 10^{14} (cm^{-3})$, corresponds to the molarity value, $1.66 \times 10^{-7} (mol \cdot kg^{-1})$, and the ion strength, I, is equal to the molarity value in case of 1:1 electrolyte. As the result of calculations, we derived $r_D = 2.9 \times 10^{-7} (m)$ and $X = 0.016$ assuming $\rho = 1.0 \times 10^3 kgm^{-3}$ and 1:1 electrolyte, and confirmed that the Coulomb potential is significantly smaller than the thermal energy in the condition discussed here.

In the above discussions, we have not taken the effect from the electric double layer at the interface into consideration. It is reported that the capacitance of the double layer at the interface between ITO and liquid crystal material (5CB) are estimated to be $15(\mu F / cm^2)$.[3] We investigated the influence from the electric double layer with the capacitance value considering an equivalent circuit of series connection between the electric double layer and liquid crystal layer, and found that there is no significant influence of the electric double layer to the theoretical curves on ε' and ε'' given in Fig.9.

CONCLUSION

We performed numerical calculations for the frequency dependence of ε' and ε'' in a low frequency range, using theoretical equations in terms of space charge polarization generated by diffusive motion of mobile ions, and found that the dielectric relaxation appears in the low frequency region and that the peak frequency for the dielectric loss factor becomes higher with decreasing the thickness of the specimen.

The thickness dependent dielectric behavior was observed in the experiment for the liquid crystal material 5CB. The observed curves for the dielectric constant and the dielectric loss factor can be successfully traced by means of curve fitting with the parameters of the diffusion coefficient and the density of the mobile ions, and we obtained $D = 4.7 \times 10^{-7} (cm^2 / s)$ and $n = 1.0 \times 10^{14} (cm^{-3})$ for the ionic impurity in 5CB at 50℃. Thus the complex dielectric constant of liquid crystal materials in a low frequency region is found to be affected by the diffusion coefficient and the density of ionic impurities.

We believe that the present method for calculating the contributions of ions to the complex dielectric constant is quite helpful for not only the analysis of a dielectric behavior of liquid crystal materials in a low frequency region but also the evaluation of the attribute of ionic impurities contained.

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