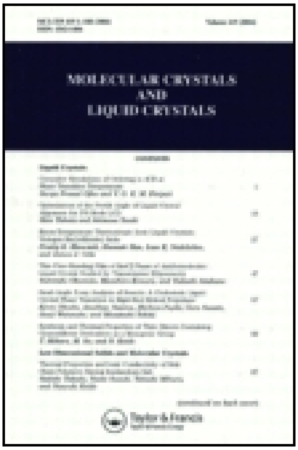

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The complex dielectric constant of a liquid crystal material, 4-cyano-4'-alkyl-biphenyl (5CB), in a low frequency region was measured by taking the thickness of a specimen as parameter. The results were analyzed by introducing an equivalent circuit of a novel concept by taking two kinds of contributions into account: one is from the electric double layer and the other is from the space charge polarization. It was found that these two effects can be distinguished by observing the dependence of dielectric dispersion on the thickness of a specimen. These measurements can be applied to a precise determination of the attributes of plural kinds of ions like the diffusion coefficient and the number density.

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

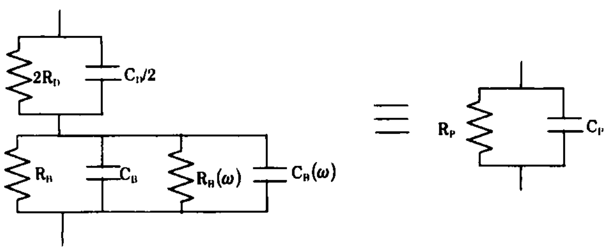
INTRODUCTION

It is known that the complex dielectric constant of liquid crystal materials increases drastically in a low frequency region. The frequency dependent property has been analyzed in terms of space charge polarization[1],[2] or from a view point of the effects of electric double layers at the electrode and bulk interface.[3] However, there seems to be no report so far that both effects are considered at the same time. Regarding the complex dielectric constant due to the space charge polarization, Uemura[4] derived theoretical expressions by solving diffusion equation of ions under an alternating electric field, and succeeded in the explanation of the anomalous increase of the complex dielectric constant of polymer materials containing ionic impurities. In the expressions, the correlation between the complex dielectric constant and the attributes of ions such as diffusion coefficient and the density is clearly defined. The expressions have also been applied to an analysis of the experimental results for liquid crystal materials and the diffusion coefficient and the density values were estimated.[1],[2] In these former studies, however, the analysis has been done by assuming the existence of only one kind of ions regarding the diffusion coefficient.

In this paper, a novel equivalent circuit will be introduced first, which is comprised of the contributions from the space charge polarization and the electric double layers, and the frequency dependent dielectric properties will be analyzed. In the second part, the analysis will be used to estimate the attributes of ions from experimental results. Here, it will be shown that the experimental results can be explained more precisely by considering the influences from plural kinds of ions in a specimen.

NUMERICAL SIMULATION OF THE FREQUENCY DEPENDENCE OF THE COMPLEX DIELECTRIC CONSTANT

It is necessary for the analysis of an anomalous increase of the complex dielectric constant to distinguish the two kinds of contributions, one is from the electric double layers and the other is from the space charge polarization. In this sense, we introduce an equivalent circuit A given in Fig.1.



Circuit A **Circuit B**

FIGURE 1 Equivalent circuit of cell injected liquid crystal materials

Circuit A : $C_B(\omega)$ and $R_B(\omega)$ represent the contribution from space charge polarization, while C_D and R_D represent the contribution from electric double layer. C_B is the capacitance controlled by the dielectric constant ε_B without the contribution from space charge polarization. R_B is the resistance controlled by conductivity σ_B representing steady state current in bulk.

Circuit B : Capacitance and resistance components to be calculated from measured complex impedance

The complex impedance, Z_A, of Circuit A is given as Eq.(1) with angular frequency, ω.

$$Z_A = \frac{2R_D}{1+(\omega R_D C_D)^2} + \frac{\dfrac{1}{R_B}+\dfrac{1}{R_B(\omega)}}{\left\{\dfrac{1}{R_B}+\dfrac{1}{R_B(\omega)}\right\}^2 + \omega^2\{C_B + C_B(\omega)\}^2}$$
$$- j\left[\frac{2\omega R_D{}^2 C_D}{1+(\omega R_D C_D)^2} + \frac{\omega\{C_B + C_B(\omega)\}}{\left\{\dfrac{1}{R_B}+\dfrac{1}{R_B(\omega)}\right\}^2 + \omega^2\{C_B + C_B(\omega)\}^2}\right] \quad (1)$$

As well for Circuit B, the complex impedance, Z_B, is given by Eq.(2).

$$Z_B = \frac{R_P}{1+(\omega R_P C_P)^2} - j\left\{\frac{\omega R_P{}^2 C_P}{1+(\omega R_P C_P)^2}\right\} \quad (2)$$

R_P and C_P can be expressed with the parameters in Circuit A by comparing the real part and the imaginary part between Eq.(1) and Eq.(2). The dielectric constant, ε', and the dielectric loss factor, ε'', are given as $\varepsilon' = C_P d / \varepsilon_o S$ and $\varepsilon'' = d / \omega\varepsilon_o R_P S$, where S the area of electrode, d the distance between electrodes, and ε_o the dielectric constant in vacuum.

The contribution from electric double layers can be estimated by numerical

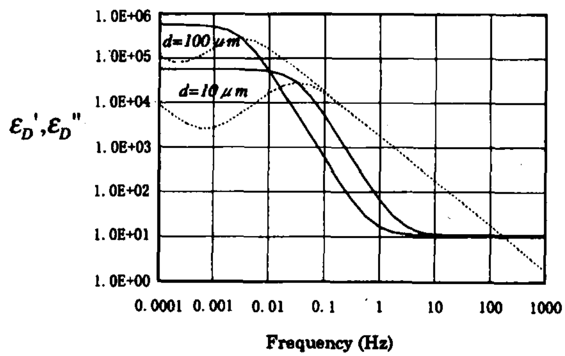


FIGURE 2 **Contributions from electric double layers to the complex dielectric constant**

Solid lines and dotted lines represent the dielectric constant ε_D' and the dielectric loss factor ε_D'' respectively.

calculation by using Eq.(1) under the condition of $R_B(\omega) \to \infty$ and $C_B(\omega) \to 0$. The frequency dependence of ε_D' and ε_D'', which correspond to ε' and ε'' values of this case, was calculated for different values of the distance d between electrodes assuming $C_D = 1\times10^{-5}(F)$, $R_D = 1\times10^{9}(\Omega)$, $\varepsilon_B = 10.9$ ($C_B = \varepsilon_o \varepsilon_B S/d$), $\sigma_B = 1\times10^{-7}(S\cdot m^{-1})$ ($R_B = d/\sigma_B S$) and $S = 1\times10^{-4}(m^2)$. Here, it is also assumed that C_D and R_D do not depend on d. The results are shown in Fig.2. The peak of ε_D'' for $d = 100\mu m$ is located at the frequency, which is one order of magnitude lower than that for $d = 10\mu m$, and the maximum value of ε_D'' is one order of magnitude larger than that for $d = 10\mu m$.

On the other hand, the theoretical expressions of the dielectric constant ε_i' and the dielectric loss factor ε_i'' representing a contribution from space charge polarization are given as Eq.(3) and Eq.(4), respectively.[4],[5]

$$\varepsilon_i' = -\left(\frac{nq^2D}{\omega\varepsilon_o kTA}\right)\left\{\frac{1+2\exp(A)\sin(A)-\exp(2A)}{1+2\exp(A)\cos(A)+\exp(2A)}\right\} \tag{3}$$

$$\varepsilon_i'' = \left(\frac{nq^2D}{\omega\varepsilon_o kT}\right)\left[1+\frac{1-2\exp(A)\sin(A)-\exp(2A)}{A\{1+2\exp(A)\cos(A)+\exp(2A)\}}\right] \tag{4}$$

where $A = d\left(\dfrac{\omega}{2D}\right)^{1/2}$

n : Density of ions、q : Electric charge、k : Boltzmann constant、
D : Diffusion coefficient of ions、T : Absolute temperature

Thus, $C_B(\omega) = \varepsilon_o\varepsilon_i' S/d$ and $R_B(\omega) = d/(\omega\varepsilon_o\varepsilon_i'' S)$ are obtained.

As are shown in Eqs.(3) and (4), ε_i' and ε_i'' depend on the distance between electrodes d. Numerical calculation for ε_i' and ε_i'' are carried out using Eqs.(3) and (4) for $d = 10\mu m$ and $100\mu m$ by inserting $D = 1.0\times10^{-11}(m^2/s)$, $n = 1\times10^{20}(m^{-3})$ and $T = 323K$. The results are shown in Fig. 3. The peak of ε_i'' for $d = 100\mu m$ is located at the frequency, which is two orders of magnitude lower than that for $d = 10\mu m$, and the maximum value of ε_i'' is two orders of magnitude larger than that for $d = 10\mu m$. Thus, it was found that the the frequency dependent properties of the dielectric constant and the dielectric loss factor by space charge polarization are different from those by electric double layers with regard to the effects of the distance between electrodes.

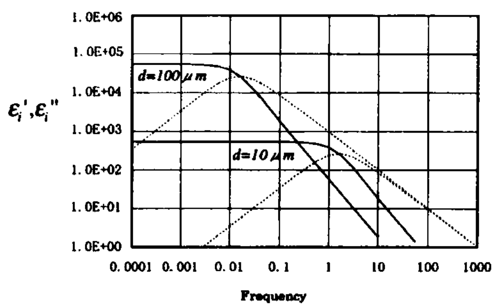


FIGURE 3 Contributions from space charge polarization to the complex dielectric

Solid lines and Dotted lines represent dielectric constants ε_i' and dielectric loss factors ε_i'' respectively.

EXPERIMENTAL

Frequency Response Analyzer (FRA) Solartron 1260 is used for measurements of the frequency dependence of the complex dielectric constant. The measurements are automatically carried out by the software MAP supplied from Toyo Corp. Keithley 428 is also utilized as a current amplifier because the input signals become too small for FRA by the increase of the impedance with decreasing frequency. 4-cyano-4'-alkyl-biphenyl (5CB), Tni=35℃, is chosen as the specimen and measurements were performed at 50℃, where it is in an isotropic liquid phase. Parallel plate glass cells with ITO, the thickness between electrodes are 9.2 μm and 44.0 μm and the area of an electrode is 1cm^2, are used for the measurement. The glass material is alkali free type 7059 from Corning.

RESULTS AND DISCUSSIONS

The experimental results for d=9.2 μm and 44.0 μm on the frequency dependent properties of ε ' and ε " and the best fitted curves by numerical calculations utilizing the equivalent circuit A are shown in Fig. 4 . The numerical calculations were carried out by assuming that the relaxation phenomenon, which appears in a higher frequency region X, is due to the contribution from the space charge polarization and the relaxation in a lower frequency region Y is due to the contribution from the electric double layers. It was found from Fig.4 that the calculated values of ε ' and ε " are in fairly good agreement with the experimental results for both d values. By the curve fittings, $D = 3.4\times10^{-11}(m^2/s), n = 1.8\times10^{20}(m^{-3})$ were obtained in the analysis of X region for d=9.2 μ m, and $D = 3.5\times10^{-11}(m^2/s), n = 1.9\times10^{20}(m^{-3})$ were obtained for d=44.0 μm. Moreover, the same value of $C_D = 1.25\times10^{-5}(F)$ was obtained in the analysis of Y region for both d=9.2 μm and 44.0 μm cases and this value is significantly close to the result obtained by Murakami[3]. The results, where no significant difference was found for the values of D, n and C_D between the two cases with different d values, support the assumption that the relaxation phenomenon in X region is due to the space charge polarization and that in Y region is due to the electric double layers.

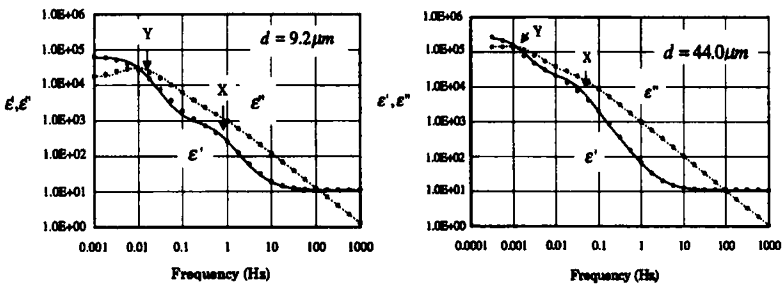


Fig.4 Frequency Dependence of the Complex Dielectric Constant of 5CB at 50℃
Closed and opened circles represent experimental values, while solid and dotted lines represent calculated values.

There exist small disagreement between the measured values and the calculated values in Fig.4. This is considered to be due to the assumption, that there exists only one kind of ions in the specimen from a view point of diffusion coefficient. Under the assumption that plural kinds of ions exist, curve fitting was carried out again for the measured values for $d = 9.2\mu m$ given in Fig.4, assuming an additivity in Eqs.(3) and (4) with regard to the contribution from each ion kind to the ε ' and ε " values.

The results are given in Fig.5. It was found that the agreement between the measured values and calculated values becomes even better than that in Fig.4 for both ε ' and ε ". From the best fitting, three sets of characteristic values of ions were obtained: (I) $D = 7.1\times10^{-11}, n = 3.9\times10^{19}$, (II)

$D = 2.0 \times 10^{-11}, n = 1.5 \times 10^{20}$, (Ⅲ) $D = 2.7 \times 10^{-12}, n = 5.4 \times 10^{20}$. The same argument was made for the case of $d = 44.0\mu m$ in Fig.4 and three sets of values were obtained: (Ⅰ) $D = 7.2 \times 10^{-11}, n = 4.5 \times 10^{19}$, (Ⅱ) $D = 2.0 \times 10^{-11}, n = 1.6 \times 10^{20}$, (Ⅲ) $D = 2.7 \times 10^{-12}, n = 3.0 \times 10^{20}$. There is no significant difference of the D value between the two cases and it seems to be reasonable to conclude that three kinds of ions exist in 5CB from a view point of the diffusion coefficient.

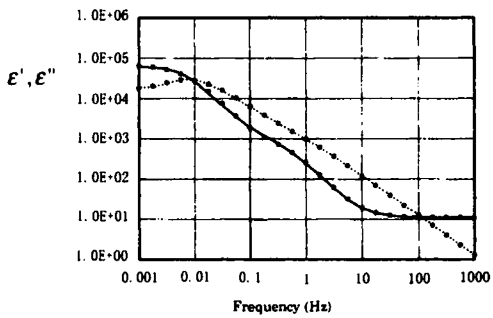


FIGURE 5 **Results by means of curve fitting introducing three kinds of ions on space charge polarization (d=9.2 μm)**

Closed circles and open circles represent measured values of the dielectric constant and the dielectric loss factor respectively, while the solid line and the dotted line represent calculated values.

CONCLUSION

The anomalous increase of the complex dielectric constant in a low frequency region can be analyzed by utilizing the equivalent circuit, considering both electric double layers and space charge polarization. Regarding the space charge polarization, a theoretical analysis, in which influences from plural kinds of ions in terms of diffusion coefficient are taken into consideration, gives a better quantitative explanation of the experimental results. By applying this analysis, attributes of three kinds of ions were obtained for a liquid crystal material, 5CB.

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References

[1] H. Naito, Y. Yokoyama, S. Murakami, M. Imai and M. Okuda, Mol. Cryst. Liq. Cryst., **262**, 249 (1995)

[2] S. Naemura and A. Sawada, Proceeding of the ASID, p127 (1997)
[3] S. Murakami, H. Iga and H. Naito, J. Appl. Phys. **80,** 6396 (1996)
[4] S. Uemura, J. Polym. Sci **10,** 2155 (1972)
[5] A. Sawada, Y. Nakazono, K. Tarumi, and S. Naemura, to appear in Mol. Cryst. Liq. Cryst. (1998)