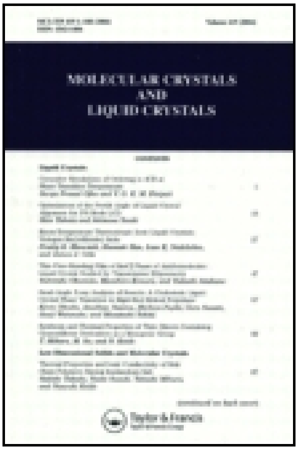

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Ion Generation in Liquid Crystals under Electric Field

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To cite this article: Shohei Naemura & Atsushi Sawada (2000): Ion Generation in Liquid Crystals under Electric Field, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 346:1, 155-168

To link to this article: http://dx.doi.org/10.1080/10587250008023875

Mol. Cryst. Liq. Cryst., 2000, Vol. 346, pp. 155-168
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Gordon and Breach Science Publishers imprint.
Printed in Malaysia

Ion Generation in Liquid Crystals under Electric Field

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Permittivity dispersion and transient current profiles of two classes of liquid crystal substances were analyzed, providing an idea of probable mechanisms of ion generation. Due to the strong local field caused by the electric double layers by ions, Schottky injection at electrodes can play an important role even under a small DC voltage application. In a higher voltage region, the dissociation of ion pairs and the recombination of free ions can be the dominant mechanisms, resulting in the Ohmic behavior of the voltage dependence of a steady-state current. Understandings of those mechanisms will be of a great help for development of advanced liquid crystal materials for uses in sophisticated displays.

Keywords: liquid crystal; ion; permittivity; transient current; Schottky effect; dissociation

INTRODUCTION

Ions are the major player in the electric conduction of nematic liquid-crystals and influence on the performance of display devices. Accordingly, not only from a scientific viewpoint but also from a practical application point of view, the ions in liquid crystals are now of great interest. Some ions are contained in liquid-crystal bulk materials from the first, and others can be generated within a liquid crystal slab between the electrodes of display panels or cells for use in electric measurements. Therefore, in order to understand what the ions are and how they behave in liquid crystal materials, it is essentially important to investigate the origin of ions, including mechanisms of ion generation under an electric field.

The behavior of mobile ions can be studied by measuring electric properties of liquid crystal materials. Experimental results were presented for liquid crystals, presumed to contain ionic impurities, to exhibit an anomalous increase in the complex permittivity in a low frequency range1-5). Theoretical considerations were also made on the space charge polarization by ions6,7), that can be applied to understand these effects of ions on the permittivity dispersion. In order to get rid of the contribution from ions generated by an applied electric field, however, care must be taken in the applied voltage. In this connection, theoretical considerations have been made on the influence of mobile ions on complex permittivities of liquid crystals under a small AC-voltage application by using the small signal perturbation theory8). The theoretical analysis provides a fairly good agreement with experimental results of the permittivity dispersion of liquid crystals in a low frequency region, which are measured under a small AC voltage application excluding influences of charge generation due to the applied field9). It has been utilized successfully to characterize several ions by their diffusion coefficients and the total quantities of electricity10).

When the applied voltage is increased, some contributions will be made from additional ions, which are generated under the applied electric field to the electric properties of liquid crystal materials. This will be noticeable when the electric current is observed under an application of a DC step-voltage. A pioneer work in this field was reported already in 1967 by G. H. Heilmeier and P. M. Heyman11) on a liquid crystal substance, PAA. Observing the transient space-charge-limited currents, they speculated that an injected electron would be captured by a neutral molecule and form a negative ion, or, alternatively, the negative ion could be directly produced by a field-dependent ionization process at the contact. From further experiments by K.Yoshino *et al.*12) on PAA and T.Yanagisawa, *et al.*13) on another liquid crystal substance, MBBA, it was considered that O^{2-} is possible to be a carrier, which captures an electron to flow into both PAA and MBBA under an electric field of 10^{6}~ 10^{7} V/m.

Many studies followed on the transient current in liquid crystals without detailed investigation to clarify the mechanisms of ion generation. G. Brere et al.(14), for example, made studies on correlation between chemical and electrochemical reactivity and dc conduction of MBBA, by observing the voltage dependence of the stationary current. The discussions, however, were mainly made on the effects of applied voltage above 300V, and, below that, it is mentioned that the behaviour is ohmic and the equilibrium is only weakly distributed by the field. It was also pointed out13) that the conduction process may be different between those space-charge-limited currents and the steady-state currents observed by G.Briere *et al.*14) in MBBA. As the steady-state current can not flow without continuous generation of charge carriers, its observation will be an effectual method to study the mechanisms of charge generation in liquid crystals.

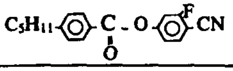
The steady-state currents were studied further in details by H.Mada *et al.*15) and S.Murakami *et al.*16) for a practical-use liquid crystal substance, 5CB. It was explained that, under an electric field below ~ 10^5 V/m, the ions causing the steady-state current was attributed to the Schottky-type charge injection due to the local electric field formed by the electric double layer on the electrode surface. Under a higher electric field, they were considered to be due to the Pool-Frenkel effect. Furthermore, the ionic impurities were attributed to the dissociation of 5CB molecules16). Similar results were obtained by the authors for another typical liquid-crystal substance, PCH-517), providing the idea that the Schottky-type charge injection is a probable mechanism within a certain voltage range. Furthermore, quantitative discussions were made by the authors on the model of ion solvation by polar liquid-crystal molecules18), which is also considered to play an important role in the ion generation in liquid crystal materials.

As briefly reviewed in the above, many studies have been made on the structures and the behavior of ions contained in liquid crystal materials. Nevertheless, further analytical and experimental works seem to be needed for various classes of liquid crystal materials, in order to fully understand the behavior of ions in these materials. In the followings, our experimental results will be presented on two classes of liquid crystal substances. Experiments were performed by combining the permittivity dispersion measurements under AC voltage application and the transient current measurements under DC voltage application. Discussions will be focused on generation mechanisms of ions and their applied-voltage dependence, especially on the effects of the voltage small enough from a practical application viewpoint.

EXPERIMENTAL

Ion Characterization by Small-Signal AC Measurements

TABLE I. Liquid crystal substances used for the experiments

Acronym	Structure
ME5N.F	
PCH-5	

The liquid crystal materials examined are listed in Table I. Test cells were prepared by using alkali-free glass substrates with an ITO electrode, and the thickness of the liquid crystal slab between the substrates is 22 μm. Sine-wave AC voltage was applied within a frequency range of 10^{-4} ~ 10^{3} Hz, and the complex permittivities were measured by using a frequency response analyzer (Solartron 1260). The permittivity dispersion was confirmed to be independent of the applied AC voltage below 0.1 V_{rms} within the frequency range, where the effect of the space charge polarization by ions are observed, and the applied voltage was fixed at 0.01 V_{rms} for the permittivity measurements. The measurements were performed in an isotropic phase at 60℃.

Examples of the measured frequency dependence of both the real part ε' and the imaginary part ε" of the complex permittivites are shown in Figs.1 and 2 by filled circles for PCH-5 and by open circles for ME5N.F. The dispersion of the dielectric constant, observed below several tens Hz in Fig.1, is due to the space charge polarization induced by mobile ions. The dispersion around 10^{-3} ~ 10^{-2} Hz range, which can be seen clearly in the relaxation profile of the dielectric loss in Fig.2, is due to the electric double layers formed by ions. A theoretical expression[8] of the dispersion of permittivities in a very low frequency range was applied, and the calculated results by using the characteristics of ions,

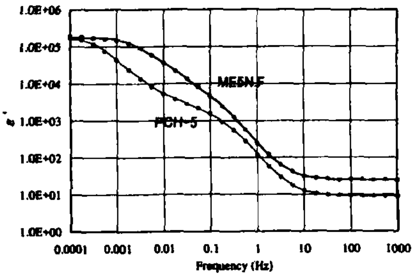


FIGURE 1 Frequency dependence of the real part ε' of the complex permittivity (60℃)
Circles: experimental, Solid lines: calculated

listed in Table II, are also shown in Figs.1 and 2 by solid lines, providing a good agreement with the measured results. At the same time, here, the equivalent circuit, shown in Fig.3, was also applied to simulate the contribution of the electric double layers[9], and the circuit parameters of the resistance R_D and C_D for the double layer were also deduced as listed in Table II.

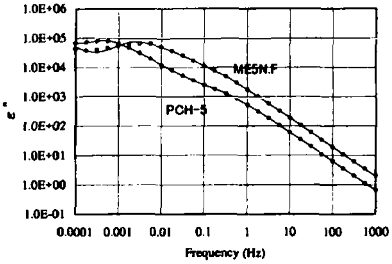


FIGURE.2 Frequency dependence of the imaginary part ε" of the complex permittivity (60℃)
Circles: experimental, Solid lines: calculated

By applying the formula,

$$\sigma_{AC} = 2\pi f \varepsilon_0 \varepsilon'', \qquad (1)$$

the measured and calculated frequency dependence of the dielectric loss ε" was converted into the frequency dependence of the AC conductivity σ_{AC} of the liquid crystal slab as shown in Fig.4. The specific resistivity SR of the liquid crystal slab under a negligibly small electric-field can be estimated from the reciprocal of the σ_{AC} value extrapolated to the condition of f = 0, providing SR=5×10^9 Ω·m for PCH-5 and SR=4×10^9 Ω·m for ME5N.F (at 60℃). It should be mentioned, however, the effect of double layers on the permittivity dispersion, which appears in the frequency range below 10^{-3} Hz, is dependent more strongly on the applied voltage than the effect of space charge polarization appearing in 10^{-2} - 10 Hz range. A typical example of the measurements is shown in Fig.5. Therefore, the deduced values of the circuit parameters of the double layer and the specific resistivity of a liquid crystal slab are those under a very small voltage application

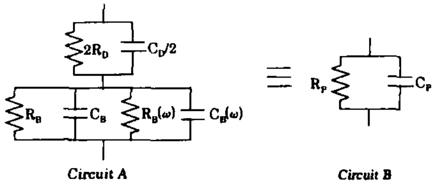


FIGURE 3 Equivalent circuit diagram to analyze the contribution from the electric double layers

(0.01V), and can not be the precise values corresponding to the condition of no applied voltage.

TABLE II. Attributes of ions contained in liquid crystal materials and parameters of the equivalent circuit (60℃)

	PCH-5				ME5N.F			
	Diffusion Coefficient D (m^2/s)	Mobility μ (m^2/Vs)	number density n (m^{-3})	Stokes radius r_s (m)	Diffusion Coefficient D (m^2/s)	Coefficient Mobility μ (m^2/Vs)	number density n (m^{-3})	Stokes radius r_s (m)
Ion (1)	1.60E-10	5.571E-09	8.80E+18	1.56E-10	1.10E-10	3.83E-09	2.20E+19	1.22E-10
Ion (2)	8.00E-11	2.785E-09	1.60E+19	3.11E-10	4.40E-11	1.53E-09	7.50E+19	3.05E-10
Ion (3)	4.90E-11	1.706E-09	2.10E+19	5.08E-10	2.30E-11	8.01E-10	1.30E+20	5.83E-10
Ion (4)	2.50E-11	8.704E-10	3.00E+19	9.96E-10	9.80E-12	3.41E-10	1.50E+20	1.37E-09
Ion (5)	1.10E-11	3.83E-10	4.30E+19	2.26E-09	3.80E-12	1.32E-10	7.20E+20	3.53E-09
Ion (6)	5.00E-12	1.741E-10	4.70E+19	4.98E-09	1.40E-12	4.87E-11	9.70E+20	9.57E-09
Ion (7)	9.20E-13	3.203E-11	4.10E+20	2.71E-08				
C_D (F)	1.70E-05				1.80E-05			
R_D (Ω)	4.55E+08				3.50E+08			
C_B (F)	4.24E-10				1.25E-09			
R_B (Ω)	3.72E+07				6.10E+06			
ε_B	9.1				25			

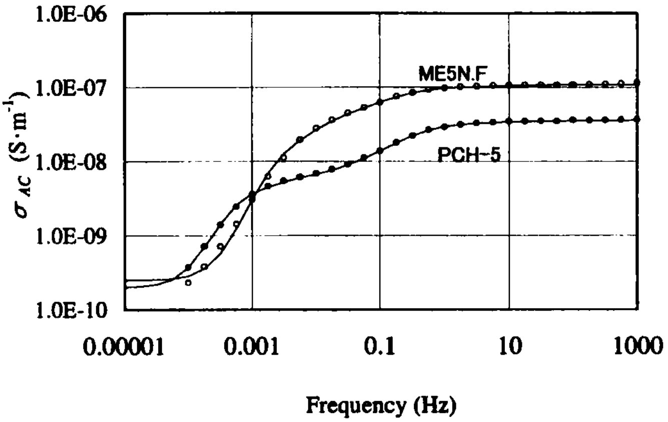


FIGURE 4 Frequency dependence of the AC conductivity, converted from Fig.2 by using Eq.(1)

Extrapolation to f=0 gives the DC conductivity; σ_{DC}= 2.5×10^{-10}S·m^{-1} for PCH-5 and σ_{DC}= 2.0×10^{-10}S·m^{-1} for ME5N.F.

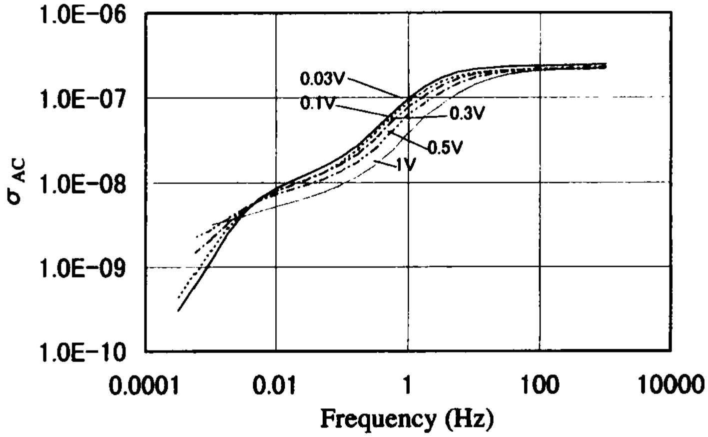


FIGURE Voltage dependence of the AC-conductivity dispersion of a liquid crystal mixture

<u>DC Voltage Dependence of Steady-State Current</u>

In order to investigate the effects of the applied electric field on the electric conducti on, measurements were made on the voltage dependence of the transient current under a DC step-voltage application, by using a digital multimeter (Keithley 6517). The results are shown in Fig.6 for PCH-5 and Fig.7 for ME5N.F. The transient current consists of an absorption current and a steady-state current. The absorption current is mainly caused by the flow of ions existing in the liquid crystal materials from the first before the voltage is applied. On the

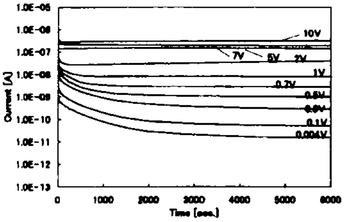


FIGURE 6 Transient current of PCH-5 at 60℃ with the applied DC voltage as a parameter

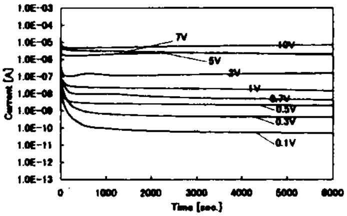


FIGURE 7 Transient current of ME5N.F at 60℃ with the applied DC voltage as a parameter

other hand, the steady-state current is caused by the charge carriers, generated under the applied voltage.

For discussions on the generation mechanisms of charge carriers in the liquid crystal slab, its resistibity values R corresponding to the steady-state current were plotted against the applied voltage values, as shown in Fig.8. Figure 8 clearly shows that there exist two regions in the measured voltage range. The first region is below 1~2 V, where the resistivity exhibits a strong dependence on the applied voltage. In the second region above 2~3 V, on the contrary, the resistivity is almost constant despite an increase of the applied voltage (Ohmic region). Plotting the logarithms of the current, log I, against $V^{1/2}$, it is found that the current is exponentially proportional to the square root of the applied voltage in the low voltage region, as shown in Fig.9.

For use in further discussions, the temperature dependence of the steady-state current was measured at two voltage values; one (0.5 V) is within the first voltage region and the other (7.0 V) the second region. As shown in Fig.10, no significant differences were found in the temperature dependence of the current between the two voltage regions.

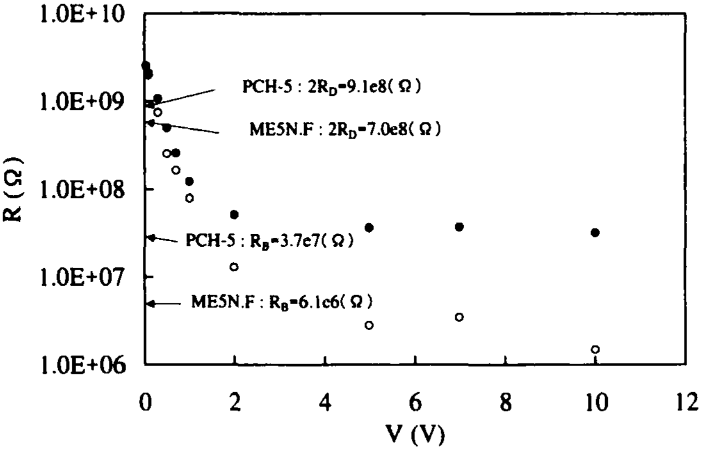


FIGURE 8 DC voltage dependence of the resistivity R (60℃)

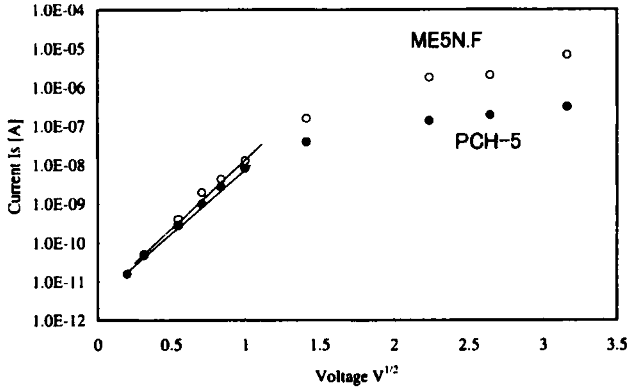


Fig.9 Logarithmic plot of the steady state current I_S against the square root of the applied DC voltage V (60℃, electrodes gap; 22 μ m)

DISCUSSIONS

When considering the ions contained in liquid crystal materials, it should be kept in mind that polar liquids are generally a good solvent for ionic substances. It can be the case of the highly polar cyano-substituted compounds of the present study. There exist some opportunities for ions to be dissolved in an isotropic or an anisotropic liquid phase of liquid crystal compounds in the material preparation process and even after the materials have been injected into the cells.

The majority of ions in number density, detected by measurements under a small AC voltage application and listed in Table II, can be those originated by dissolution. Judging from the Stokes radius, those ions are most probably inorganic ions, naked or hydrated, and solvated ions with polar molecules as the solvent[17]. Moreover, the electrolytic dissociation can not be ignored as one of the ion generation mechanisms in cases of polar liquid crystal substances. The generated ions also have good chances to be stabilized by forming solvated ions.

The SR values in the order of 10^9 Ω·m at 60℃ are generally accepted as those of insulating liquids. Nevertheless, taking account of the above possibilities for ions to be contained in liquid crystal materials and the measured concentration of several tens ppb, the liquid crystal slab between plate electrodes would be properly treated as an extrinsic semiconductor layer not as an intrinsic semiconductor or a pure insulating liquid.

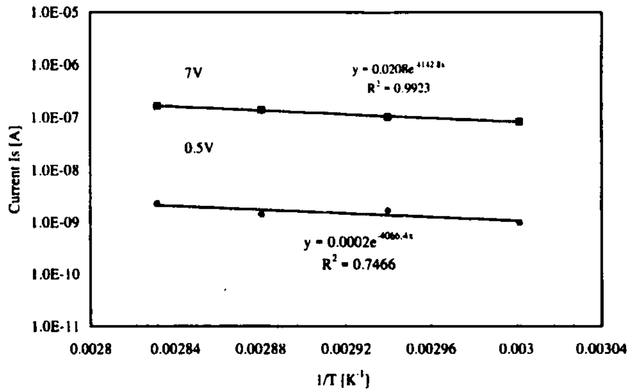


FIGURE 10 Temperature dependence of the steady state current in PCH-5 (60℃)

The electric double layer, formed by the space charges (ions) in the interface layer of the liquid crystal slab and the surface charges of the ITO electrode, will decrease the energy levels of electrons in the liquid crystal slab and introduce the Schottky barrier. The electron affinity was calculated to be 0.4 eV for PCH-5 and 0.9 eV for ME5N.F, providing an estimated barrier height ϕ_{LC} of around 3.8 to 4.3 eV from ITO side, by assuming that the work function of ITO in the vacuum is 4.7 eV as used commonly.

The barrier is lowered by the Schottky effect by $\Delta\phi$, given by

$$\Delta\phi = e_0\,[e_0 E/(4\pi\,\varepsilon_0\,\varepsilon_r)]^{1/2}, \tag{2}$$

where e_0 is the electronic charge, ε_0 is the free space permittivity, ε_r is the relative dielectric coefficient and E is the local electric-field strength at the interface. Combining Eq.(2) with the Richardson equation yields for the current I_S

$$I_S = AT^2 \exp[(-\phi_{LC} + \Delta\phi)/k_B T], \tag{3}$$

where A is the Richardson-Dushman coefficient, k_B is the Boltzmann constant and T is the absolute temperature. The validity of Eq.(3) for the present system is supported qualitatively by the obtained applied-voltage dependence of the current, shown in the low voltage region ($V \lesssim 1$ Volt) in Fig.9, assuming that the internal field strength E in Eq.(2) is proportional to the applied voltage V. This assumption is valid when almost all the applied voltage is allotted to the double layers, and this seems to be the case of the present system, judging from the R_D values, which are larger than the R_B values by more than one order of magnitude as listed in Table II.

Equation (3), together with Eq.(2) and the formula, $E=V/2d_D$ (d_D: thickness of the double layer), enables to estimate the d_D value by using the measured relative dielectric coefficient values of the liquid crystal substances as ε_r in Eq.(2). The thickness d_D was calculated as 1.5 nm for PCH-5 and 0.5 nm for ME5N.F. The value of PCH-5 is similar to the reported value of 1.4 nm for 5CB[16]. Nevertheless, when considering the expected applied-voltage dependence of the double-layer structure, it seems to be essentially important for further quantitative discussions to investigate the structure of double layers and the diffusion potential within the barrier region more precisely.

The barrier height ϕ_{LC} can also be calculated by Eq.(3) from the measured temperature dependence of the current, which is shown in Fig.10. They are 0.56 eV for PCH-5 and 1.10 eV for ME5N.F, which do not correspond to the above values of around 4 eV of the present liquid-crystal molecules. The calculated ionization potential values of 9.72 eV for PCH-5 and 9.79 eV for ME5N.F do not seem to fit, either. Most probable explanation of this lowered barrier would be the energy levels introduced by the ionic impurities. In other words, charge transfer is taking place at the interface between electrodes and ions in liquid crystal materials.

Charge transfer at the electrode causes neutralization of ions and removes some ions from the liquid crystal slab, yielding the formula,

$$dC_{ion}/dt = -\mu_{ion}(EC_{ion}/d)\,, \tag{4}$$

where C_{ion} is the number density of total free ions, μ_{ion} is the mobility of the ions and d is the thickness of the liquid crystal slab. Assuming that free ions are generated by dissociation at the rate k_{ion} and recombine with the coefficient k_r, the following equation is valid in the steady state;

$$k_{ion} - k_r C_{ion}^{\,2} - \mu_{ion}(EC_{ion}/d) = 0\,. \tag{5}$$

As the current density is given by,

$$J = \mu_{ion} C_{ion} E \tag{6}$$

combining Eq.(5) and Eq.(6) yields,

$$k_r d J^2 + \mu_{ion}{}^2 E^2 J - k_{ion} \mu_{ion}{}^2 E^2 d = 0 . \tag{7}$$

The current density J is given by,

$$J = -(1/2d\,k_r)\,\mu_{ion}{}^2 E^2 + \mu_{ion} E\,[(\mu_{ion}{}^2 E^2) / (4 d^2 k_r{}^2) + (k_{ion}/k_r)]^{1/2} . \tag{8}$$

When Schottky-type injection at electrodes proceeds further as the applied voltage increases, the neutralization of ions is enhanced at the interface and the effect of the double layers becomes negligible. This results in a uniform internal field, E=V/d, throughout the liquid crystal slab without interfacial regions. In this voltage region, no neutralization at electrodes by Schottky injection occurs any more, and the generation and the recombination of free ions are the dominant mechanisms of the change of ion density. In this case, J is approximated as

$$J = \mu_{ion} E\,(k_{ion}/k_r)^{1/2} \quad , \tag{9}$$

by neglecting the second term of Eq.(7). This linear relation between J and E corresponds to Ohm's law, which is rather clearly found for PCH-5 in the higher voltage region in Fig.8. The resistivity of PCH-5 in this plateau region agrees well with the R_B value of $3.7 \times 10^7\,\Omega$, which was obtained from the permittivity dispersion measurements and listed in Table II. Dissociation energy was obtained as 1.64 eV for PCH-5, by using the temperature dependence of the conductivity and the viscosity of the liquid crystal material measured independently.

The resistivity of ME5N.F is lower than PCH-5, as is also shown in Fig.8. This can be due to the smaller energy of dissociation for the solute molecules, resulting in higher degree of dissociation. The dissociation energy value, which can be applicable to quantitative discussions, however, was not obtained due to the scattered results of the measurements. The resistivity values of ME5N.F fluctuate a bit around the R_B value of $6.1 \times 10^6\,\Omega$, and exhibit a further decreasing tendency at 10 V. This is due to some chemical reaction at electrodes, which was observed in the experiments. It is not clear whether this is an abnormal case of the sample used in the present experiments or a general case of this system. Further experiments will be performed by using different metal electrodes.

CONCLUSIONS

Even though there still remains some uncertainty, Schottky effect is considered to be the most probable mechanism of the charge transfer at the electrode surface in a low voltage region. The electric field strong enough to induce the Schottky injection of electrons will be easily formed by electric double layers caused by the ions contained in a liquid crystal slab. The structure of the double layer is dependent to the applied voltage, which was qualitatively observed by the permittivity dispersion measurements in a very low frequency region.

The Schottky barrier height is considered to be a subject to the ions contained in a liquid crystal slab, which will introduce many trap levels in the electron energy levels of the band structure. In this sense, the polar liquid crystal substances in the present study, whose specific resistivity under no applied field was deduced to be in the order of 10^9 $\Omega\cdot$m at 60℃, are considered properly to be categorized as an extrinsic semiconductor rather than a pure insulating liquid. As a consequence, the voltage dependence of the steady state current in the low voltage region does not show a significant material dependence, as far as the presently used cyano-substituted liquid crystals are concerned.

The injected electrons neutralize the ions in the interfacial region of the liquid crystal slab, and consequently the effect of the double layer decreases as the applied voltage increases. The dependence of the steady-state current on the applied voltage becomes less than the exponential proportionality to the square root, and becomes constant (Ohmic) in a higher voltage region.

In the Ohmic region, the generation of free ions due to the dissociation of ion pairs and their recombination become the major mechanism to maintain the flow of a constant number of free ions. Most probably due to the relatively higher concentration of the electrolyte solute and the relatively higher degree of dissociation, the ester substance, ME5N.F, exhibits a bit larger amount of free ions than PCH-5.

Understandings of the generation mechanisms of ions and their behavior are quite important for the development of advanced liquid crystal materials especially for uses in sophisticated displays. In this connection, further studies will be proceeded to clarify the structure of electric double layers and its applied-voltage dependence.

ACKNOWLEDGMENTS

The authors wish to express their appreciation to their colleagues of LC R&D from Merck Japan Ltd. and Merck KGaA, Germany, for their experimental works and useful discussions.

Part of this work was performed under the management of ASET in the MITI's R&D Program supported by NEDO.

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