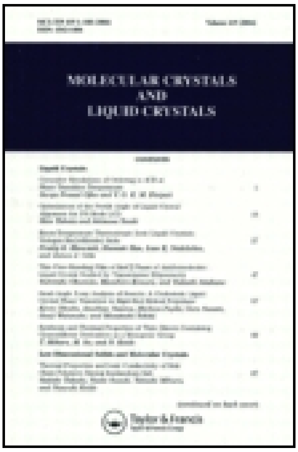

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Observation of Adsorption and Desorption Processes of Impurity Ions in Nematic Liquid Crystal Cells

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OBSERVATION OF ADSORPTION AND DESORPTION PROCESSES OF IMPURITY IONS IN NEMATIC LIQUID CRYSTAL CELLS

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Abstract A method for studying adsorption and desorption processes of impurity ions in nematic liquid crystal cells is proposed. The experimental results for 4-cyano-4'-pentyl biphenyl are interpreted in terms of a rate-equation approach and the time constants for the adsorption and desorption processes of the ions are determined.

§1. INTRODUCTION

Recently, the transport mechanisms of the impurity ions in nematic liquid crystals (NLCs) have been studied with transient current techniques and impedance spectroscopy$^{1-5)}$. This stems mainly from the fact that impurity ions in NLCs crucially influence the device performance of NLC displays. However, the adsorption and the desorption phenomena of impurity ions in NLC cells have not been examined yet.

In this paper, we present a novel method for the measurement of the adsorption and desorption processes of the impurity ions in NLC cells and analyze our experimental data in terms of a rate equation approach.

§2. PRINCIPLE OF THE METHOD

The adsorbed ions onto electrodes or alignment layers are induced by applying a voltage pulse to the NLC cells because the impurity ions are drifted toward the electrodes and then are accumulated at the interface between the electrode and NLC. The amount of the adsorbed ions can be calculated from the decrease in the ac conductivity of the NLC cells. This is because the ac conductivity of 4-cyano-4'-pentyl biphenyl (5CB) has been shown to be proportional to the bulk impurity ion density in the low frequency regime[5] and the adsorbed ions do not contribute to the ac conductivity. The representative behavior of the ac conductivity of 5CB before, during and after a voltage pulse is shown in Fig.1. For the calculation of the bulk ion density and hence the adsorbed ion density, we have measured the drift mobility of the ion at various temperatures with the time-of-flight method, and found that the sign and the magnitude of the drift mobility of the impurity ions are positive and 4.3×10^{-6}cm^2/Vs at 313K, respectively, for example.[6]

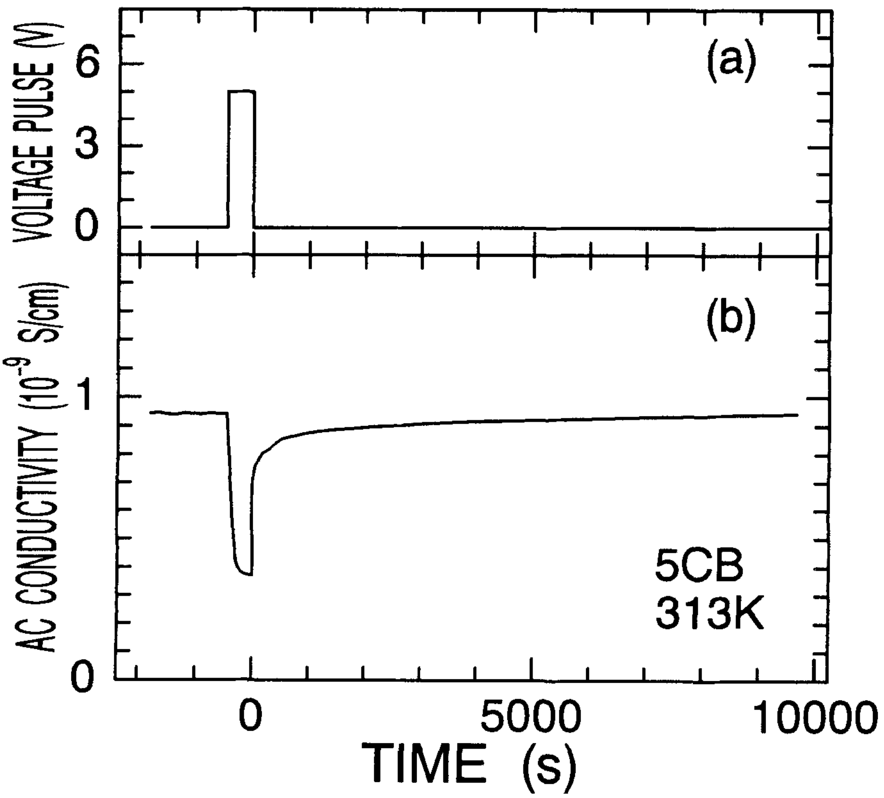

Figure 1 (a) Voltage pulse applied to a 5CB NLC cell.
Figure 1 (b) The representative behavior of the ac conductivity of a 5CB NLC cell before, during and after the voltage pulse at 313K.

We postulate the following rate equation for the description of the adsorption and desorption processes of the impurity ions:

$$\frac{dn_a(t)}{dt} = b_t\Big[N - n_a(t)\Big]n_f(t) - b_r n_a(t) \tag{1}$$

where n_a is the adsorption ion density, N is the maximum adsorption ion density, n_f is the free ion density at the interface between the electrode and NLC, and b_t and b_r are the adsorption and desorption rate constants, respectively.

The above equation is approximately solved for the adsorption process during the voltage pulse application:

$$n_a(t) = N\left\{1 - \exp\left(-\frac{t}{\tau_a}\right)\right\} \tag{2}$$

and for the desorption process after the voltage pulse application:

$$n_a(t) = n_{a_0}\exp\left(-\frac{t}{\tau_b}\right) \tag{3}$$

where $\tau_a{=}1/(b_t n_f)$ and $\tau_b{=}1/b_r$. Our experimental data are analyzed by means of the above solutions.

§3. EXPERIMENT

Homogeneously aligned NLC cells were used in this experiment. The thickness of the cell and the area of the electrode were 22μm and 2cm^2, respectively. The NLC used was 5CB, which has positive dielectric anisotropy $\Delta\epsilon \simeq 10$. The ac conductivity of the NLC cell was measured with a lockin amplifier at 10Hz and at constant temperatures. The adsorbed ions were induced by the application of a voltage pulse to the cell and were measured before, during and after the application of the voltage pulse. The height of the voltage pulse was 5V.

§4. RESULTS AND DISCUSSION

First, we observe the adsorption process of the impurity ions onto the electrode induced by the voltage pulse. Figure 2 shows a plot of the adsorbed ion densities, which were determined from the ac conductivity at t=0 in Fig.1, vs the width of the voltage pulses, t_p. The inset in Fig.2 shows a replot of Fig.2; the x-axis of Fig.2 is displayed on a logarithmic scale in the inset. The adsorbed ion density is almost zero below ~ 0.5s, but increases above that time. It is important to point out that the time is well corresponding to the ion transit time at 313K. This correspondence clearly indicates that the adsorption of the ions takes place after the accumulation of excess ions by the applied voltage pulse. It can be seen in Fig.2 that the adsorbed ion density increases linearly with time and then becomes constant. We fit Eq.(2) to the experimental data in Fig.2 and obtain τ_a=4s and $N=2.0\times10^{12}\text{cm}^{-2}$, which is in the range of the observed surface charge density on a solid surface (10^{11}-10^{13}cm^{-2}).[7]

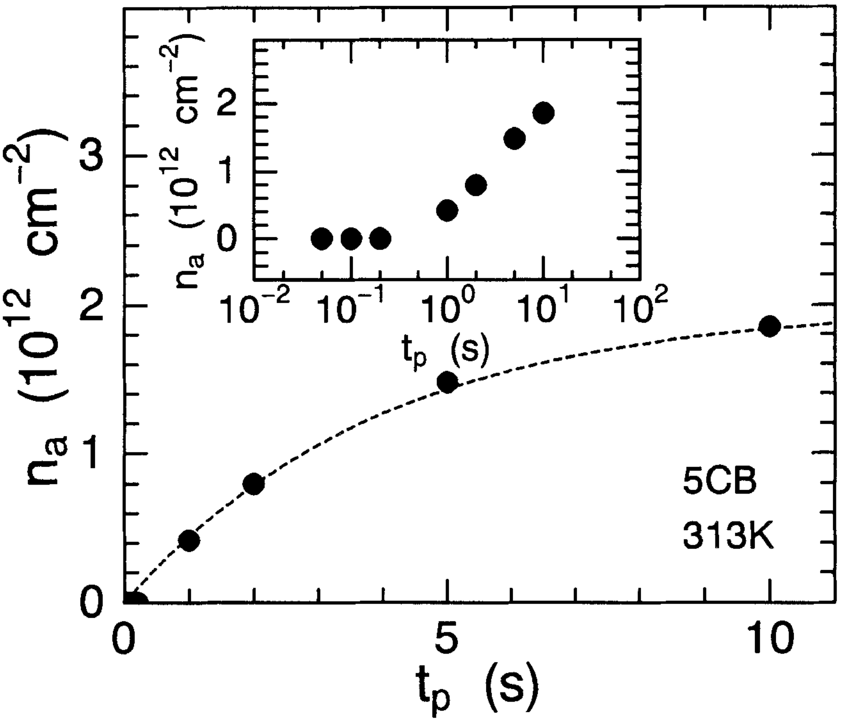

Figure 2 A plot of the adsorbed ion densities n_a, which were determined from the ac conductivity at t=0 in Fig.1, vs the width of the voltage pulses t_p for the 5CB cells at 313K. The dotted line is fitting of the adsorbed ion density by the function of the form, $n_a(t) = N\left\{1-\exp\left(-\frac{t}{\tau_a}\right)\right\}$: $N=2.0\times10^{12}\text{cm}^{-2}$ and τ_a=4s. The inset shows a replot of this figure; the x-axis displayed on a logarithmic scale in the inset.

Second, we observe the desorption process of the ions from the electrode after the voltage pulse application. Figure 3 shows a semilogarithmic plot of the adsorbed ion density vs the time after the voltage pulse is ceased. The adsorbed ion density decreases owing to the desorption. The decay of the adsorbed ion density is exponential and is characterized by two time constants (τ_{b_1}=90s and τ_{b_2}=2400s at 313K), suggesting that there are two kinds of the adsorption sites on the electrode surfaces.

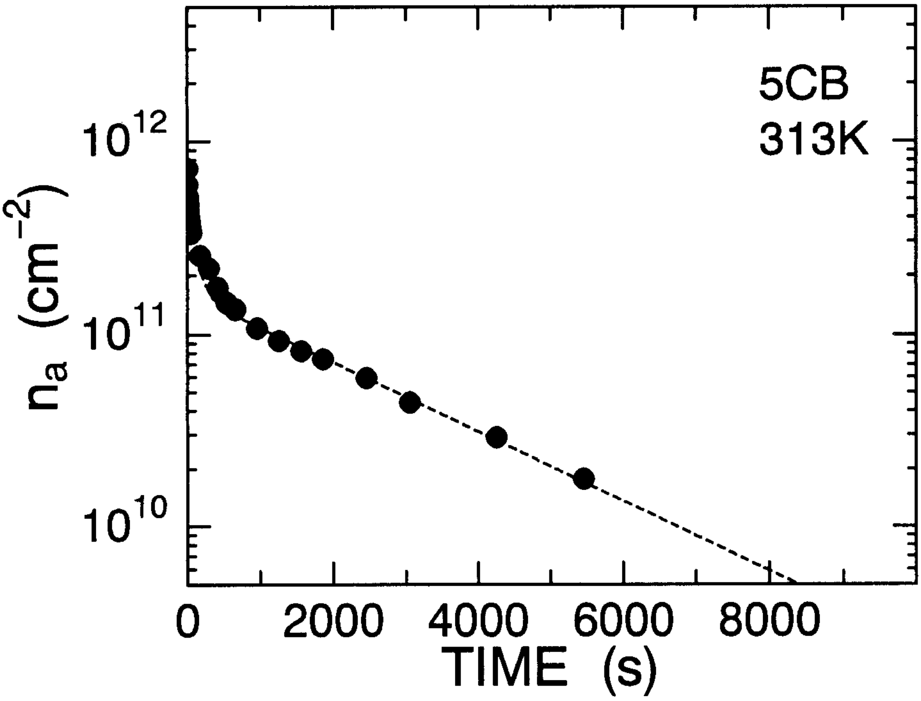

Figure 3 A semilogarithmic plot of the adsorbed ion density vs the time after the voltage pulse is ceased for the 5CB cell at 313K. The dotted line is fitting of the adsorbed ion density by the function of the form, $n_a(t) = n_{a_1} \exp\left(-\frac{t}{\tau_{b_1}}\right) + n_{a_2} \exp\left(-\frac{t}{\tau_{b_2}}\right)$: n_{a_1}=3.5×10^{11}cm^{-2}, n_{a_2}=1.7×10^{11}cm^{-2}, τ_{b_1}=90s and τ_{b_2}=2400s.

Finally, we show the temperature dependence of the time constants (τ_a, τ_{b_1} and τ_{b_2}) in Fig.4. The time constant, τ_a, is temperature independent, and hence no barrier is formed for the adsorption. On the other hand, τ_{b_1} and τ_{b_2} are strongly depenent on temperature and the activation energies for τ_{b_1} and τ_{b_2} are 1.0eV and 0.7eV, respectively. The activation energy is generally determined by the strength of the interaction between adsorbate and surface such as physical adsorption (mainly van der Waals interaction) and chemisorption.[8] The magnitude of these activation energies is much higher than that expected in case of van der Waals interaction.[9]. Thus, we conclude that chemical bonds are very likely formed between the impurity ions and the electrode surfaces.

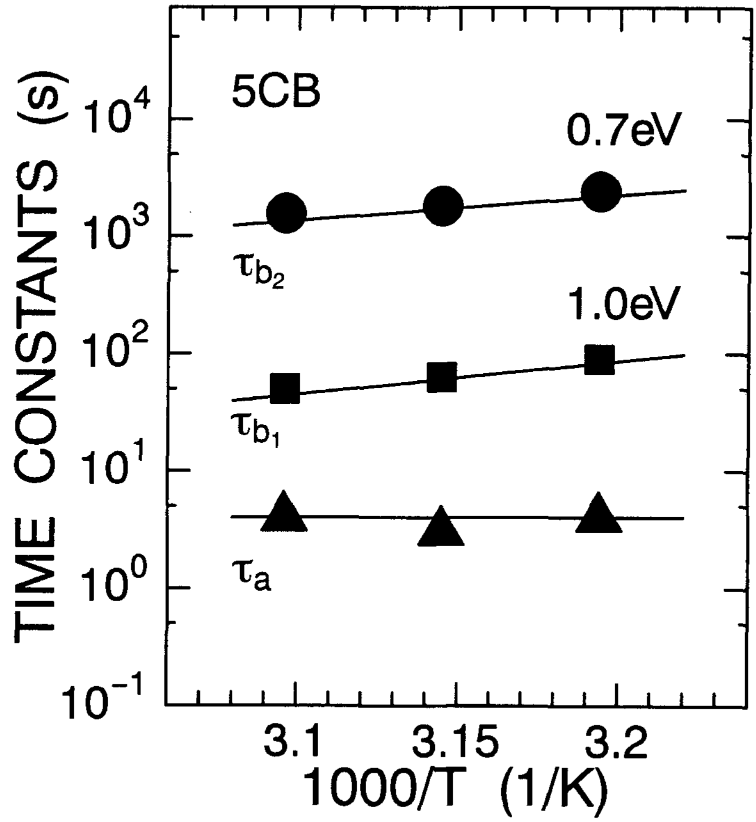

Figure 4 Temperature dependence for τ_a, τ_{b_1} and τ_{b_2} for the 5CB cell. The activation energies of τ_{b_1} and τ_{b_2} are determined to be 1.0eV and 0.7eV, respectively.

§5. CONCLUSIONS

We have proposed the method for measuring the adsorption and desorption processes of the impurity ions in NLC cells by monitoring ac conductivity of the cells. We find that the adsorption and the desorption processes can be explained with the rate equation, Eq.(1). The time constant of the adsorption process and the density of maximum adsorption sites are determined from Eq.(2) to be 4s and $2\times10^{12}\mathrm{cm}^{-2}$ at 313K, respectively. The desorption processes are chracterized by two time constants (τ_{b_1}=90s and τ_{b_2}=2400s at 313K). The activation energies for τ_{b_1} and τ_{b_2} are 1.0eV and 0.7eV, respectively, indicating that the interaction between the impurity ions and the electrode surface is due to chemisorption rather than van der Waals interaction.

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