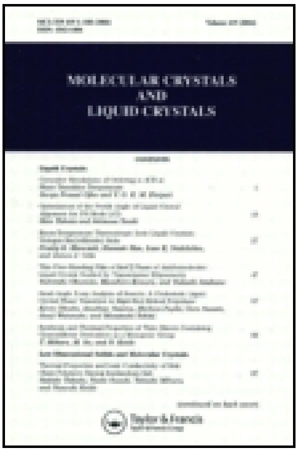

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Desorption Processes of Adsorbed Impurity Ions on Alignment Layers in Nematic Liquid Crystal Cells

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DESORPTION PROCESSES OF ADSORBED IMPURITY IONS ON ALIGNMENT LAYERS IN NEMATIC LIQUID CRYSTAL CELLS

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Abstract The desorption processes of adsorbed impurity ions on various alignment layers in nematic liquid crystal cells have been studied by measuring ac conductivity of the cells. The liquid crystal used here is 4-cyano-4'-pentyl biphenyl. The adsorption of the ions is induced by the application of dc voltage to the cells. It is found in all alignment layers that the adsorbed ions decay exponentially after the cessation of the dc voltage application, and that the time constants of the decay exhibit thermally activated behavior. It is shown that the desorption process is governed by the surface energy of the alignment layers.

INTRODUCTION

The influence of impurity ions in nematic liquid crystal (NLC) cells has been extensively studied.[1–3] The studies have been motivated by the fact that the impurity ions often degrade the device performance of NLC displays.[4] In particular, the adsorbed ions on alignment layers play a key role of the degradation in applying dc signals to NLC displays.

In this paper, we observe the desorption processes of adsorbed impurity ions in 4-cyano-4'-pentyl biphenyl (5CB) cells for five types of alignment layers by measuring ac conductivity of the cells. A dominant factor controlling the desorption processes is then examined.

REVIEW OF THE METHOD

We have proposed a method for measuring the absorption and desorption processes of impurity ions.[5] We review here the principle of the method. The impurity ions are adsorbed onto either electrodes or alignment layers by applying a dc voltage pulse to 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 NLC cells; the ac conductivity of 5CB has been shown to be proportional to the bulk impurity ion density at low frequencies[2] and the adsorbed ions do not contribute to the ac conductivity. The typical behavior of the ac conductivity of 5CB before, during, and after a voltage pulse is shown in Figure 1. For the calculation of the bulk ion density and hence the adsorbed ion density from the ac conductivity, we have measured the drift mobility of the ion at various temperatures with the time-of-flight method, and found that the sign and magnitude of the drift mobility of the impurity ions are positive and 4.3×10^{-6} cm^2/Vs at 313 K, respectively.[3]

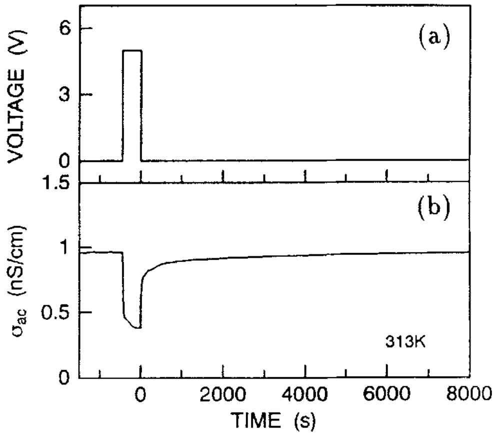


FIGURE 1 (a) Voltage pulse applied to a 5CB cell. (b) The typical temporal variation in the ac conductivity of the 5CB cell at 313K.

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

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

where n_a is the adsorbed ion density, N is the maximum adsorption site density on alignment layers, 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 can be solved for the adsorption process (during the voltage pulse application) in case where n_f is regarded as being constant,

$$n_a(t) = N[1 - \exp(-t/\tau_a)], \tag{2}$$

and for the desorption process (after the cessation of the voltage pulse application) in case where re-adsorption of desorbed ions is neglected,

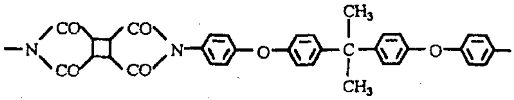
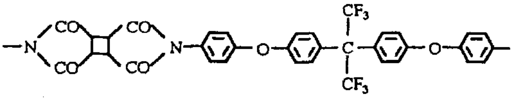
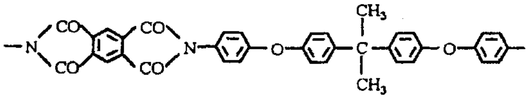
$$n_a(t) = n_{ao}\exp(-t/\tau_b), \tag{3}$$

where $\tau_a = 1/(b_t n_f)$ and $\tau_b = 1/b_r$. We have shown that Equations (2) and (3) successfully explain the experimental data[5], and in the present paper the desorption processes are analyzed by Equation (3).

EXPERIMENT

Homogeneously aligned NLC cells were prepared for the present experiment. The thickness of the cells and the area of the electrode were 5-22 μm and 2 cm^2, respectively. NLC used was 5CB, which has positive dielectric anisotropy, $\Delta\epsilon \simeq 10$. Alignment layers of poly(vinyl alcohol) (PVA) and polyimides (PI-A, PI-B, PI-C; the chemical formulae are listed in Table I) were coated onto indium tin oxide (ITO) electrodes. NLC cells without alignment layers were also fabricated. The ac conductivity of the NLC cells was measured with a lockin amplifier at 10 Hz as a function of temperature. The adsorbed ions were induced by the application of a voltage pulse to the cell, and the density of the adsorbed ions was measured before, during, and after the application of the voltage pulse. The height and duration of the voltage pulse were 5 V and 5 s, respectively. The wetting angles were measured for ITO, PVA, PI-A, PI-B, and PI-C to determine their surface energies.

TABLE I Chemical formulae of repeat units of polyimides used in this study.

Alignment layer	Repeat unit
PI-A	
PI-B	
PI-C	

RESULTS AND DISCUSSION

We study the desorption processes of different alignment layers. Figure 2 shows a semilogarithmic plot of the adsorbed ion density on PVA alignment layer vs time after the voltage pulse is ceased. The temporal variation in the adsorbed ion density due to the desorption is characterized by two exponential decays. We examined the cell thickness dependence of the two exponential decays, and found that the fast decay is dependent on the cell thickness while the slow decay is not. If the temporal variation in the ac conductivity is due solely to the desorption, it is expected that the decay is independent of the cell thickness. For this reason, we focus ourselves on the observation of the slow decay process. The fast decay would result from the diffusion process of accumulated ions near the interface between NLC and the alignment layer toward the NLC bulk. Other alignment layers except for PI-B whose decay process is shown in Figure 2 exhibit the decay similar to that of PVA.

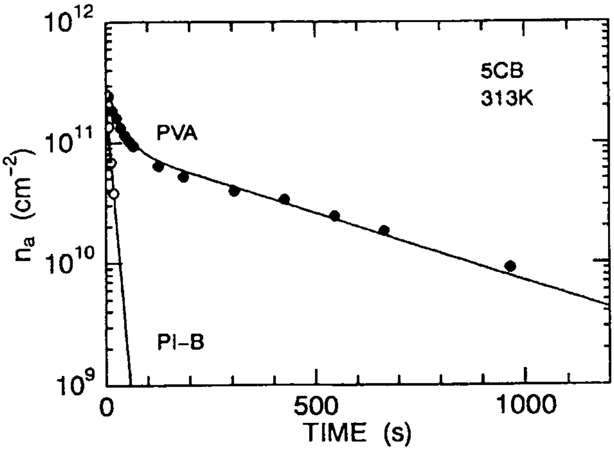


FIGURE 2 A semilogarithmic plot of the adsorbed ion density vs the time after the voltage pulse is ceased for the 5CB cells with PVA and PI-B alignment layers measured at 313 K.

The desorption processes of different alignment layers have been measured as a function of temperature, and we have found that the time constant τ of the slow decay shows the thermally activated behavior, and hence is expressed as $\tau = \tau_o \exp(\Delta E/kT)$, where τ_o is the pre-exponential factor, ΔE is the activation energy, k is the Boltzmann constant, and T is the temperature.[5] Although the slow decay was not observed for PI-B layer, we tentatively set ΔE=0 for PI-B layer.

To obtain information concerning a key factor in the desorption process, we studied the properties of alignment layers such as surface energy and dipole moment. Through the study, we found a good correlation between ΔE and the surface energy for the alignment layers. The result is shown in Figure 3. We understand the correlation as follows: ΔE can be regarded as the van der Waals interaction energy between the ions in 5CB and the surface of the alignment layer. The surface energy equals half the energy needed to separate two flat surfaces from contact to infinity.[6] Since the surface energy is essentially the van der Waals energy between the two surfaces, ΔE can be related to the surface energy via the combining laws of the Hamaker constants.[6]

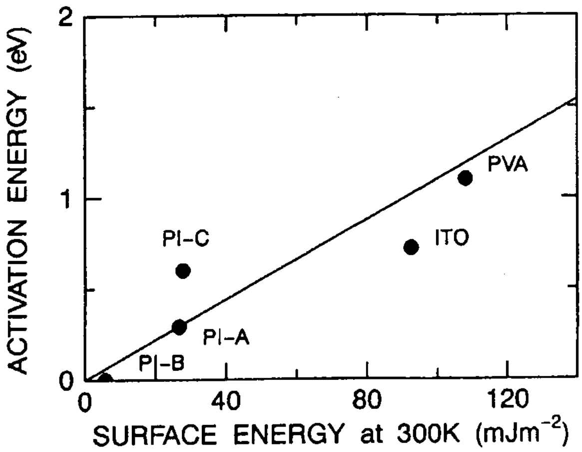


FIGURE 3 A plot of the activation energy of the desorption process vs the surface energy for five alignment layers. The units : mJm^{-2} and eV are the practical usage of those of surface energy and activation energy, respectively.

It is important to stress that an alignment layer with low surface energy lead to rather a fast desorption process. We believe that this finding is valuable information for the design of LC displays.

CONCLUSIONS

We have studied the desorption processes of adsorbed impurity ions in 5CB for different alignment layers by monitoring ac conductivity of the NLC cells. The desorption processes are thermally activated. We find that the activation energy increases with surface energy of the alignment layers. A physical origin of this finding is suggested in case where the van der Waals interaction between the ions and the surface of the alignment layers operates. We stress that the surface energy of an alignment layer is a key factor in controlling the adsorption process of impurity ions in LC.

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