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Dynamics of molecular exchange between aligning adsorbed film of liquid crystal and the bulk

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The liquid crystal (LC) originally filled in thin cells is replaced by a different LC having a drastically different pretilt angle. The mechanism of desorption/adsorption of LC molecules from/on the adsorbed LC film at the substrate changes the composition of the adsorbed layer and thus the pretilt angle. The time dependence of molecular pretilt angle at solid surfaces of homogeneously aligned LC cells is measured. The characteristic molecular exchange time depends on the coefficients of desorption of the first LC. The results presented here provide an important insight into the molecular exchange between solid surface and bulk fluid. © *2008 American Institute of Physics*.
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Anchoring properties of liquid crystals (LCs) are determined by the anisotropy of the alignment layer[1] and its interaction with the LC bulk. Regardless of the aligning material used, a layer of LC molecules is adsorbed on to the aligning surface and contributes to the anchoring of bulk LC. The anchoring energy W, due to the adsorbed molecules, is of the order of $10^{-5}-10^{-7}$ J m^{-2}. It is comparable to the anchoring energy of LCs on rubbed polyimide and photoaligning layers.[2,3] Therefore, the contribution of the adsorbed LC film is important, and in some cases, it solely determines the alignment of LC on the boundary surface as well as the alignment memory effect,[4,5] light-induced anchoring,[3] and magnetically induced alignment.[6,7] However, this phenomenon remains poorly understood. Ouchi *et al.* and Vetter *et al.*[8,9] explained the observed weakening of magnetically induced alignment as being due to increased rotational diffusion of the adsorbed LC molecules upon heating. Recently, we reported[10] that the anchoring energy of an adsorbed layer in a magnetically aligned cell decreased after thermal treatment. We established the dependence of this decrease on the changes in the angular distribution of the adsorbed molecules caused by molecular exchange between the adsorbed layer and the LC bulk, i.e., adsorption (desorption) of bulk LC molecules on to (from) the adsorbed alignment layer. The experimentally measured temperature dependence of the anchoring energy allowed us to estimate the activation barrier, $\Delta E \approx 2.16$ eV, for the process between LC pentylcianobiphenyle (5CB) on indium tin oxide (ITO) surface and the probability of desorption, $A_- \approx 6 \times 10^{-6}$ s^{-1}, of these molecules at room temperature.

Here, we report experimental proof of intensive molecular exchange between the adsorbed alignment film and the LC bulk. The experiment monitors the dynamics of the pretilt angle of *one* LC (LC-1) on a layer of the adsorbed molecules of *another* LC (LC-2). The pretilt angles, θ_{ii} ($i=1,2$), of each LC on a layer of adsorbed molecules of the same LC are different. (Here, the first subscript denotes the

"bulk" LC molecules and the second subscript denotes LC molecules adsorbed on the aligning surface.) Therefore, in cells in which aligning surfaces are formed via adsorption of LC-1 molecules and which are filled with LC-2, the molecular exchange between the adsorbed layer and the bulk should result in a gradual change of the pretilt angle. Desorption of LC-1 molecules and their dispersion into the bulk of LC-2 followed by reverse adsorption of LC-2 molecules eventually results in the replacement of the adsorbed layer of LC-1 by the layer of LC-2 and, correspondingly, a change in the pretilt angle from $\theta_{1,2}$ (of LC-1 molecules on a layer of LC-2) to $\theta_{2,2}$. To the best of our knowledge, the experiments described here, with an *in situ* exchange of molecules between a solid surface and bulk fluid, have never been reported. This experiment became possible due to long-range orientational interactions in the nematic phase, which render this method highly sensitive to the alignment of the LC and anchoring conditions.

To clearly prove intensive molecular exchange between aligning surface and LC bulk, we needed to find an aligning layer that provided essential difference in the pretilt for two different LCs. Seo observed a large difference in the pretilt angle of 5CB and ZLI-4792 on a fluorinated polyimide layer.[11] Therefore, we chose the same LCs but the fluorinated polyimide poly(2,6-piperazinedione) (PPZD) based on 5-perfluorooctyl-1,3-phenylenediamine as the aligning layer. This polyimide was synthesized according to example 8 in Ref. 12 where a high pretilt for ZLI-4792 ($>20°$) was reported. This polyimide is quite different from the one in Seo's paper, mainly in the position of the fluorinated branch on the polyimide molecule, which results in a different pretilt angle for 5CB and ZLI-4792.

We used planar cells made from ITO coated glass substrates. Inner surfaces of the glass substrates were covered with alignment layers of polyimide PPZD. The polyimide coated surfaces were rubbed and then assembled in to a cell in antiparallel configuration which provided homogeneous alignment of both the LCs. The thickness of the cell, $L = 50$ μm, was controlled with the help of internal polymer

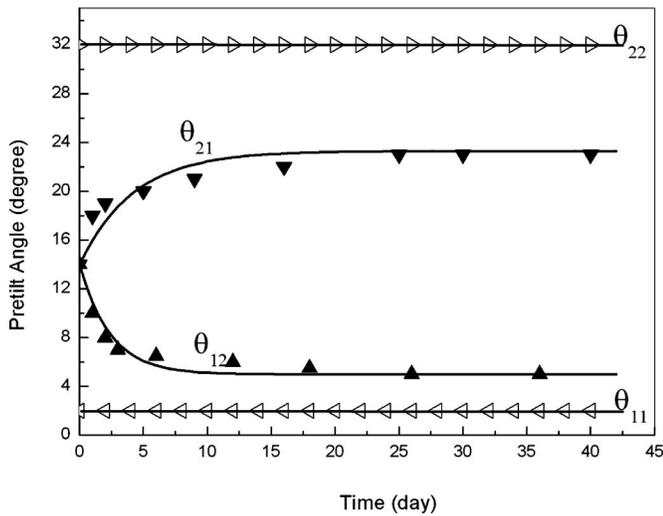a)Electronic mail: satyen@xray.kent.edu.

FIG. 1. Time dependence of $\theta_{1,2}$ (up triangles), $\theta_{2,1}$ (down triangles), $\theta_{1,1}$ (left triangles), and $\theta_{2,2}$ (right triangles) after refilling the cells.

spacers. Three sides of the cells were sealed by UV-curable epoxy, and the fourth side was left open.

The cells were heated to temperatures above the clearing point of LCs ($T_c \approx 34$ °C for 5CB and $T_c \approx 92$ °C for ZLI-4792) and filled by capillary action. Optical observation under a polarizing microscope showed homogeneous alignment of both LCs. Pretilt angles were measured by the magnetic null method.[13] The pretilt angles of LC 5CB and ZLI-4792 were found to be stable in time and had values of $\theta_{1,1} = 2°$ and $\theta_{2,2} = 32°$, respectively.

After the measurements of pretilt angles $\theta_{1,1}$ and $\theta_{2,2}$, the LC was removed from the cells by vacuum suction. The cells were refilled with a different LC, i.e., the cell with LC-1 was refilled with LC-2 and vice versa. Immediately after refilling, we measured the same values of the pretilt in both types of cells, i.e., $\theta_{2,1} \approx \theta_{1,2} = 14° \pm 1°$. These values were in the middle of the $\theta_{1,1}$ and $\theta_{2,2}$ and they changed with time. The pretilt in the cell refilled with LC-1, $\theta_{1,2}$ approached the value $\theta_{1,1}$ and the pretilt in the cell refilled with LC-2, and the value $\theta_{2,1}$ evolved toward $\theta_{2,2}$ with time, as shown in Fig. 1.

The observed behavior of pretilt angles is naturally explained by a gradual replacement of the adsorbed LC molecules of, e.g., the LC-1 by molecules of LC-2 from the latter's bulk. One may expect to obtain the values of the pretilt in the refilled cells to achieve values of $\theta_{1,1}$ and $\theta_{2,2}$ in the two cases after equilibration. However, that is not the case. The pretilt angles always fall short of the expected values of $\theta_{1,1}$ and $\theta_{2,2}$, suggesting an incomplete "exchange" of the two types of LC molecules. In fact, it is due to incomplete removal of LC-1 from the cell by vacuum suction. To estimate the amount of the initial LC remaining in the cell, the clearing temperatures T_c before and after the refilling were recorded. We found that after refilling the cell with 5CB, the clearing temperature was $T_{c,1,2} = 39.8$ °C instead of 34.2 °C. Similarly, after refilling of the cell with ZLI-4792, the clearing point was found to be 80.3 °C instead of 92 °C. These values were compared with measured dependence of $T_c(\alpha_m)$ on the mole fraction α_m of 5CB in ZLI-4792, which was linear and very well fitted to $T_c = \alpha_m T_{c,1,1} + (1 - \alpha_m) T_{c,2,2}$. From this, we estimated the mole fraction of residual 5CB in ZLI-4792 to be $\alpha_{m,1} \approx 0.2$ and the mole frac-

tion of residual ZLI-4792 in 5CB to be $\alpha_{m,2} \approx 0.1$. These values are not negligible and obviously influence the pretilt angles, such that $\theta_{2,1} < \theta_{2,2}$ and $\theta_{1,2} > \theta_{1,1}$.

To describe the change of the pretilt angles after refilling, we propose that it depends linearly on the relative concentration of LC molecules in the bulk and in the adsorbed layer. The pretilt angle at the adsorbed layer can be written as

$$\theta = \tilde{\theta}_{1,1}\alpha_{1v}\alpha_{1s} + \tilde{\theta}_{2,2}\alpha_{2v}\alpha_{2s} + \tilde{\theta}_{1,2}\alpha_{1v}\alpha_{2s} + \tilde{\theta}_{2,1}\alpha_{2v}\alpha_{1s}. \quad (1)$$

Here, $\tilde{\theta}_{1,2}$ is the pretilt angle of the pure LC-1 at the adsorbed layer of LC-2 molecules, $\tilde{\theta}_{2,1}$ is the pretilt angle of the pure LC-2 on the adsorbed layer of LC-1 molecules, and $\tilde{\theta}_{1,1} \equiv \theta_{1,1}$ and $\tilde{\theta}_{2,2} \equiv \theta_{2,2}$ are the pretilt angles of pure LC-1 and LC-2 on the adsorbed layer of the same LC. The terms α_{1v} and α_{1s} represent the relative concentrations of LC-1 molecules in the bulk and in the adsorbed surface layer. Similarly, α_{2v} and α_{2s} are the corresponding relative concentrations of LC-2, $\alpha_{1v} + \alpha_{2v} = 1$, and $\alpha_{1s} + \alpha_{2s} = 1$. These relative concentrations are approximately equal to their corresponding mole fractions.

In the case of cells filled with pure LC-1, the coefficients $\alpha_{2v} = \alpha_{2s} = 0$, $\alpha_{1v} = \alpha_{1s} = 1$, and $\theta = \tilde{\theta}_{1,1} = 2°$. Analogously, for a cell filled with LC-2, $\theta = \tilde{\theta}_{2,2} = 32°$. Filling a cell which was initially filled with LC-1 with LC-2 should result in $\alpha_{2v} = 0.8$, $\alpha_{1s} = 1$, $\alpha_{1v} = 0.2$, $\alpha_{2s} = 0$, and $\theta = 14°$. Substituting these values in Eq. (1), we obtain that $\tilde{\theta}_{2,1} = 17°$. Alternatively, the cell with adsorbed molecules of LC-2 and filled with LC-1 is expected to have $\alpha_{1v} = 0.9$, $\alpha_{1s} = 0$, $\alpha_{2v} = 0.1$, $\alpha_{2s} = 1$, $\theta = 14°$, and $\tilde{\theta}_{1,2} = 12°$.

The dynamics of the pretilt angle θ is determined by the exchange of molecules between the LC bulk and adsorbed layers. This process is described by the kinetic equations for adsorption (desorption) of LC molecules on (from) adsorbed layer. For the case of a cell refilled with LC-1,

$$\frac{d\alpha_{1s}}{dt} = -A_1\alpha_{1s} + \alpha_{1v}(\alpha_{1s}A_1 + \alpha_{2s}A_2), \quad (2)$$

where A_1 and A_2 are the probabilities of desorption of LC-1 and LC-2 molecules, respectively. During the derivation of this equation, we assumed that the coefficients of adsorption for both LCs are equal. Therefore, the amounts of adsorbed LC are proportional to the relative concentrations α_{1v} and α_{2v}. Since the concentration of LC molecules in the bulk is much higher than in adsorbed film, the term α_{1v} is expected to be constant. The molecular exchange between the bulk and the adsorbed layer after refilling with LC-2 can also be written in the same manner.

The solution of Eq. (2) reads,

$$\alpha_{1s}(t) = (\alpha_{1s,0} - \alpha_{1s,\text{inf}})\exp[-(\alpha_{1v}A_2 + \alpha_{2v}A_1)t] + \alpha_{1s,\text{inf}}, \quad (3)$$

where $\alpha_{1s,0}$ and $\alpha_{1s,\text{inf}}$ are the concentrations of the LC-1 in the adsorbed layer immediately after refilling and after infinitely long period of time, respectively,

$$\alpha_{1s,\text{inf}} = \frac{\alpha_{1v}A_2}{\alpha_{1v}A_2 + \alpha_{2v}A_1}. \quad (4)$$

The expression (1) together with Eqs. (3) and (4) describes the dynamic of the pretilt angle $\theta_{1,2}(t)$. One can see that, in our simplest model, the time dependence $\theta_{1,2}(t)$ is
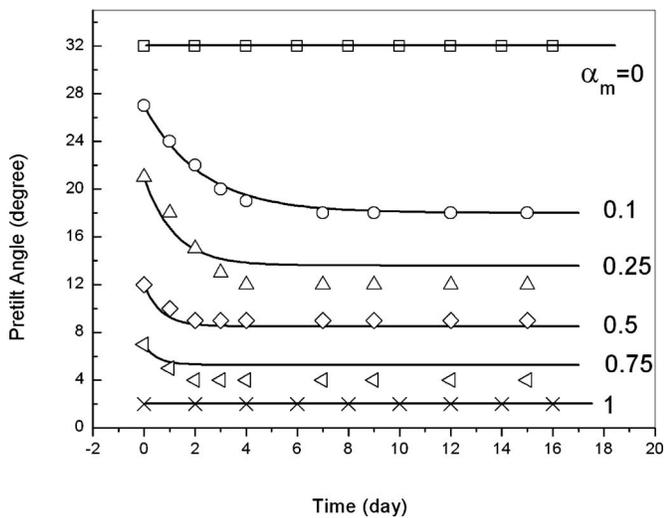
FIG. 2. Time dependence of the pretilt angle of the mixture of 5CB and ZLI-4792 after the cell is refilled for different molar ratios α_m of the two compounds.

described by an exponent with the characteristic time $\tau_{1,2} = (\alpha_{1v}A_2 + \alpha_{2v}A_1)^{-1}$. The expression for the time dependence $\theta_{2,1}(t)$ is also analogous.

The time dependences $\theta_{1,2}(t)$ and $\theta_{2,1}(t)$, calculated for $\widetilde{\theta}_{1,1} = 2°$, $\widetilde{\theta}_{2,2} = 32°$ and $\widetilde{\theta}_{1,2} = 12°$; $\widetilde{\theta}_{2,1} = 17°$, are presented by the solid lines in Fig. 1. For $\theta_{1,2}(t)$, the experimental parameters $\alpha_{1v} = 0.9$ and $\alpha_{1s} = 0$ were used, while for $\theta_{2,1}(t)$, they were $\alpha_{1v} = 0.2$ and $\alpha_{1s} = 1$. The coefficients of desorption for LC-1 ($A_1 = 8.7 \times 10^{-6}$ s^{-1}) and for LC-2 ($A_2 = 5.8 \times 10^{-6}$ s^{-1}) were calculated from the decay time $\tau_{1,2}$. From the time dependence $\theta_{2,1}(t)$, the fits gave $A_1 = 2.5 \times 10^{-6}$ s^{-1} and $A_2 = 5.8 \times 10^{-6}$ s^{-1}, in very good agreement with the calculated value.

As one can see from Fig. 1, the characteristic times $\tau_{1,2}$, $\tau_{2,1}$ are very long. Therefore, one can expect, unlike one-component nematics, the duration for the establishment of a stationary state in LC cell to be long. To verify this expectation, we prepared a number of mixtures that consisted of LC-1 (5CB) and LC-2 (ZLI-4792) in different molar fractions and monitored the dynamic of the establishment of an equilibrium state of the pretilt. The experimental data are presented in Fig. 2 together with theoretical fits. These fits were obtained using Eqs. (1)–(4), the desorption coefficients $A_2 = 2.9 \times 10^{-5}$ s^{-1} and $A_1 = 1.3 \times 10^{-6}$ s^{-1} were the fitted parameters. As we expected, the establishment of equilibrium state of the pretilt for 5CB was fast; we did not observe significant changes about 10 min after the cells were filled. Also, we did not observe any long term changes in the pretilt of ZLI-4792 perhaps because of its eutectic character. In the case of the mixture of LC-1 (5CB) and LC-2 (ZLI-4792), the

achievement of the stationary state lasts for 1–5 days depending on the relative fraction of LCs in the mixture. It should be noted that the estimated values $A_2 = 2.9 \times 10^{-5}$ s^{-1} and $A_1 = 1.3 \times 10^{-6}$ s^{-1} are of the same order as, but different from, the values that we obtained from the dynamics of $\theta_{1,2}(t)$ and $\theta_{2,1}(t)$. This fact deserves further investigations. At present, we can presume that the desorption coefficients depend on the relative concentration of LC-1 and LC-2 molecules and their arrangement on the surface.

In summary, we were able to see the effects of molecular exchange between the adsorbed layer and the LC bulk from the measured time dependence of the pretilt angle of one LC on the adsorbed layer of another LC. The characteristic times of the changes in the pretilt angle depended on the coefficients of desorption of LC molecules from the adsorbed layer. The exchange of molecules between the bulk and the adsorbed layer leads to an equilibrium value of the pretilt angle which depends on the relative concentration of the two LCs in the cell. The experiments described here provide an insight into the process of molecular exchange between the adsorbed surface layer and bulk fluid.

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