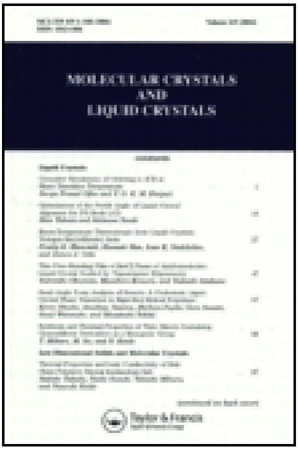

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Surface Control of Dye Adsorption in Liquid Crystals

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Surface Control of Dye Adsorption in Liquid Crystals

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We develop the kinetic model of the dye adsorption in LC cells. The motion of dye molecules is considered as Brownian diffusion in the potential field, created near the surfaces due to the Van-der-Waals and electrostatic interactions, as well as specific liquidcrystalline effects, caused by the orientational and translational order parameter changes. On the boundaries, the adsorption and desorption processes are taken into account with coefficients, which depend on the surface density of adsorbed dyes. The model shows that dark adsorption depends mainly on surface parameters, which determine the stationary adsorption and the relaxation time. Light irradiation reduces the surface barrier and increases the adsorption and desorption coefficients. As the result all of the processes are strongly intensified and the characteristic time of light-induced adsorption becomes essentially shorter than the time of dark adsorption. Dark and light-induced adsorptions depend on the director field because the surface orientation of LC affects the surface barrier and the adsorption/desorption coefficients.

Keywords: liquid crystal; dye adsorption; kinetics; light-induced effects

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INTRODUCTION

Liquid crystals (LCs) have been extensively studied in recent years as media for optical processing and storage. The photoinduced reorientation of dye doped LC caused by dye adsorption, is one of the most promising new photoeffects[1-4].

The main features of dye adsorption are the following:

- The dye adsorption can occur without light irradiation. However, this adsorption, which is referred below as dark, is rather slow and its characteristic time $\tau \sim 10^4 s$ is much larger than the bulk diffusion time $\tau_D = L^2/D \sim 10 \div 10^2 s$, where L is a cell thickness ($L \sim 10 \div 50 \mu m$) and D is a diffusion coefficient ($D \sim 10^{-11} \div 10^{-10} m^2/s$). The dark adsorption causes the fact that cell prehistory without irradiation affects significantly on the light-induced effect[5].
- The characteristic time of the light-induced effects $\tau \sim 10^3 s$ is significantly smaller than for dark adsorption but still larger than τ_D.
- Both the dark dye adsorption and the light-induced dye adsorption depend drastically on the polar orientation of LC on the surface (the orientation effect for the light-induced dye adsorption can not be reduced to the simple polarization dependence of light absorption)[4].

The goal of this paper is to develop the kinetic model of dye adsorption in LC cells. The model is based on the following:

- The motion of dye molecules is considered as Brownian diffusion in the potential field, created near the substrates.
- On the boundaries the adsorption and desorption processes are taken into account with coefficients, which depend on the surface density of adsorbed dyes.
- Light irradiation reduces the surface barrier and increases the adsorption and desorption coefficients intensifying strongly the adsorption process.
- The orientation effect occurs because the polar orientation of LC on the surface affects the surface barrier and the adsorption/desorption coefficients.

In this paper, we do not consider light-induced azimuthal reorientation effects, thus we only study the kinetic processes of the dye adsorption in cells with homogeneous director fields.

MODEL

Let us consider the motion of dye molecules in the liquidcrystalline matrix as one-dimensional diffusion in the potential field $U(x)$, so their distribution function $P(x,t)$ is described by the equation:

$$\frac{\partial P(x,t)}{\partial t} = \frac{\partial}{\partial x}\left\{D(x)\left[\frac{1}{kT}\frac{\partial U}{\partial x}+\frac{\partial}{\partial x}\right]\right\}P(x,t), \qquad (1)$$

For electrically neutral molecules the potential field is constant in the bulk and can be set to zero. This potential is essentially non zero only near the substrates due to the Van-der-Waals and electrostatic multipole interactions, as well as the specific liquidcrystalline effects, caused by the orientational and translational order parameter changes. The order parameter changes can also alter the diffusion coefficient $D(x)$ near the surfaces. These surface regions are rather thin compare to the cell thickness L, so it is reasonable to consider separately the solutions of Eq.(1) in three regions: in the bulk region B (Fig. 1) with $U_0 = 0$ and $D = D_0$, and in two thin regions S_1 and S_2 near the substrates. The thickness of the adsorbed dye films are assumed negligibly small, so the total thickness of these regions is L. Continuity of concentrations $\tilde{P}_i(t) = P(v_i, t)$ and of flows $\tilde{J}_i(t) = \mp J(v_i, t)$ on the interfaces $x = v_i$ between the bulk region and the i-th surface regions $(v_1 = d, v_2 = L - d)$ provides the boundary conditions for Eq.(1) in these regions. Here and below the upper sign corresponds to the first substrate and the lower sign corresponds to the second substrate. The signs of the dye flows in the surface regions are chosen in such way that the adsorption process provides the positive contribution (Fig.1).

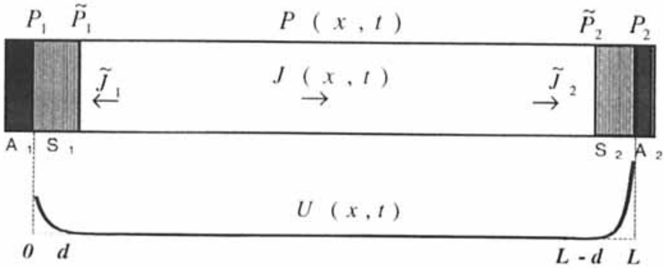

FIGURE 1. Schematic representation of dye adsorption processes and in a LC cell.

The **surface regions (S_1, S_2)** are much thinner than the film thickness and have very short relaxation times, so the adiabatic approach is applicable and the flows in the surface regions remain homogeneous because of $\frac{\partial P(x,t)}{\partial t} = -\frac{\partial J(x)}{\partial x} = 0$. Therefore, the dye distributions in the surface regions are controlled by the quasi-stationary flows on the i-th substrate $J_i(t) = \tilde{J}_i(t)$.

$$\frac{\partial P(x,t)}{\partial x} + \frac{1}{kT}\frac{\partial U(x)}{\partial x} P(x,t) = \pm J_i(t)/D(x) \tag{2}$$

Solution of the Eq.(2) reads [6]:

$$P(x,t) = e^{\frac{U(u_i)-U(x)}{kT}} \left[P_i(t) \pm \int_{u_i}^{x} e^{\frac{U(x')-U(u_i)}{kT}} J_i(t)/D(x')dx' \right] \tag{3}$$

where $u_1 = 0$, $u_2 = L$, and $P_i(t) = P(u_i, t)$ is the concentration near the i-th substrate. Solution (3) provides equation between $\tilde{P}_i(t)$, $P_i(t)$ and $J_i(t)$:

$$\tilde{P}_i(t) = \frac{P_i(t)}{w_i} + \frac{\tilde{d}_i J_i(t)}{D_0} \tag{4}$$

where $\tilde{d}_i = \left| \int_{u_i}^{v_i} e^{\frac{U(x)}{kT}} D_0/D(x)dx \right| = s_i d / w_i$ is the effective diffusion thickness of surface regions, which can be much larger than actual thickness d, $w_i = \exp\{-U(u_i)/kT\}$ is the Boltzmann factor for the surface potential, s_i is a dimensionless coefficient, which depends on the profiles of $U(x)$ and $D(x)$.

The flows $J_i(t) = \frac{\partial A_i}{\partial t} \equiv \dot{A}_i$ control the surface densities of adsorbed dyes A_i, and are determined by adsorption and desorption processes on the substrates:

$$J_i(t) = \alpha_i(A_i)P_i(t) - \beta_i(A_i) \tag{5}$$

where $\alpha_i(A_i)$ is the adsorption coefficient and $\beta_i(A_i)$ is the desorption coefficient on the i-th substrate, which both depend on A_i. The explicit forms of these dependencies will be discussed later.

In the **bulk region** $D(x) = D_0$ the equation (1) reduces to the standard diffusion equation:

$$\frac{\partial P(x,t)}{\partial t} = D_0 \frac{\partial^2 P(x,t)}{\partial x^2}, \tag{6}$$

The boundary conditions on the interfaces $x = v_i$ are provided by the continuity of concentrations $\tilde{P}_i(t)$ and flows $\tilde{J}_i(t)$. Their combination with Eq.(4) and Eq.(5) results in:

$$P(v_i, t) \mp G_i(A_i) \left. \frac{\partial P(x,t)}{\partial x} \right|_{x=v_i} = C_i(A_i) \tag{7}$$

where $G_i(A_i) = \tilde{d}_i + \frac{D_0}{w_i \alpha_i(A_i)}$, and $C_i(A_i) = \frac{\beta_i(A_i)}{w_i \alpha_i(A_i)}$.

Equation (6) with boundary conditions (7) can be solved numerically for any $\tilde{d}_i, w_i$, $\alpha_i(A_i)$, and $\beta_i(A_i)$. However, the flows in the real system are weak and quasistationary, resulting in the homogenous depletion $\frac{\partial P(x,t)}{\partial t} = const$. Thus the space dye distribution in the bulk has a parabolic form with coefficients, which can obtained from flow continuity on the boundaries and the conservation law for dye molecules:

$$P(\tilde{x},t) = -\frac{\tilde{x}^2}{2D_0 \tilde{L}}\left(\dot{A}_1 + \dot{A}_2\right) + \frac{\tilde{x}}{D_0}\dot{A}_1 + \frac{1}{\tilde{L}}(\Sigma - A_1 - A_2) - \frac{\tilde{L}}{6D_0}\left(2\dot{A}_1 - \dot{A}_2\right) \tag{8}$$

where $\tilde{x} = x - d$, $\tilde{L} = L - 2d$, $\Sigma = \int_0^L P(x,0)dx$ is the number of dye molecules in the cell per unit area. Combining Eq.(7) and Eq.(8) we obtain the kinetic equations for the surface densities of adsorbed dyes A_i (we substitute $\tilde{L}$ with L because $L >> d$):

$$\left(6g_i(A_i) + 2\right)\dot{A}_i - \dot{A}_{3-i} = 6\tau_D^{-1}\left(\Sigma - A_1 - A_2 - LC_i(A_i)\right) \quad i = 1,2 \tag{9}$$

where $g_i(A_i) = G_i(A_i)/L$. The zeros of right sides of Eqs.(9) determine the condition for stationary bulk density $\overline{P}$ and surface densities of adsorbed dyes $\overline{A}_i$:

$$\overline{\overline{P}} = \frac{\Sigma - \overline{A}_1 - \overline{A}_2}{L} = \overline{C}_1 = \overline{C}_2 \tag{10}$$

where

$$\overline{C}_i = C_i(\overline{A}_i) = \frac{\beta_i(\overline{A}_i)}{w_i \alpha_i(\overline{A}_i)}. \tag{11}$$

Linearization near $\overline{A}_i$ reduces Eq.(9) to the system of homogeneous differential equations respect to $\tilde{A}_i$ $\left(\tilde{A}_i = A_i - \overline{A}_i\right)$:

$$(6\overline{g}_i + 2)\dot{\tilde{A}}_i - \dot{\tilde{A}}_{3-i} = -6\tau_D^{-1}\left[(1 + L\overline{C}_i')\tilde{A}_i + \tilde{A}_{3-i}\right] \qquad i = 1,2 \tag{12}$$

where $\overline{g}_i = g_i(\overline{A}_i)$ and $\overline{C}_i' = \left.\frac{\partial C_i(A_i)}{\partial A_i}\right|_{A_i = \overline{A}_i}$.

The solution of Eq.(12) exhibits exponential relaxation to the stationary state with two characteristic times $\tau_{1,2}$. We will calculate $\tau_{1,2}$ later for the specific cases that correspond to dark adsorption and light-induced adsorption.

Before we present the results of our calculations, let us consider the possible dependencies for $\alpha_i(A_i)$ and $\beta_i(A_i)$. When A_i is small, almost all dye molecules are adsorbed on the bare substrate with the corresponding adsorption coefficient $\alpha_0^{(i)}$. When A_i becomes large, additional dye molecules are adsorbed on the substrate, which has been already covered with the dye molecules and the adsorption coefficient has another value $\alpha_\infty^{(i)}$. We approximate $\alpha_i(A_i)$ as:

$$\alpha_i(A_i) = \alpha_\infty^{(i)} + (\alpha_0^{(i)} - \alpha_\infty^{(i)}) \cdot \exp\{-\sigma_i A_i\} \tag{13}$$

where σ_i is a fitting parameter, which should be roughly about area per one molecule. For desorption we use the similar approximation, taking into account that there is no desorption from the bare substrate:

$$\beta_i(A_i) = \beta_\infty^{(i)}[1 - \exp\{-h_i A_i\}] \tag{14}$$

where h_i is another fitting parameter, which should have the same order of magnitude as σ_i.

RESULTS AND DISCUSSION

Dark (symmetric) adsorption.

Often a LC cell has the same substrates. In this case, the surface parameters in absence of irradiation are equal and we can omit indexes $w_i = w$, $g_i(A_i) = g(A_i)$, $C_i(A_i) = C(A_i)$, etc. According to (10), the symmetric stationary surface density of adsorbed dyes should exist $\overline{A}_1 = \overline{A}_2 = \overline{A}$. The relaxation solution (Eq.(12)) to this stationary state splits on the symmetric and antisymmetric parts:

$$\tilde{A}_i = A_+ \exp(-t/\tau_+) \pm A_- \exp(-t/\tau_-) \qquad i = 1,2 \qquad (15)$$

where A_+ and A_- are constants, which depend on the initial distribution, and where τ_+ and τ_- are the relaxation times:

$$\tau_+ = \tau_D \frac{1/6 + \overline{g}}{2 + L\overline{C}'} \qquad \tau_- = \tau_D \frac{1/2 + \overline{g}}{L\overline{C}'} \qquad (16)$$

The antisymmetric relaxation time τ_- determines the stability of the symmetric stationary state. Once $\overline{C}' < 0$ this state becomes unstable and new non-symmetric stationary state ($\overline{A}_1 \neq \overline{A}_2$) appears. However, the analysis of the equation (11) shows that $\overline{C}' < 0$ requires rather specific conditions ($\alpha_0 << \alpha_\infty$ and $\sigma < h$)). Normally $\overline{C}' > 0$, and thus the state antisymmetric part is negligible, because of a small asymmetry of the initial distribution.

The symmetric relaxation in the system is controlled by τ_+, Eq.(16). The denominator in τ_+ depends on $\overline{A}$. For small $\overline{A}$ ($\overline{A} \le h^{-1}, \sigma^{-1}$) $\overline{C}' \cong \overline{C}/\overline{A}$ and equation (10) results in $2 + L\overline{C}' \cong \Sigma/\overline{A}$. For large $\overline{A}$ ($\overline{A} \ge h^{-1}, \sigma^{-1}$) $\overline{C}' \to 0$.

Usually in the experiments without irradiation $\tau \equiv \tau_+ >> \tau_D$, this concludes that

$$\overline{g} = \frac{sd + \overline{\lambda}}{wL} >> 1, \qquad \overline{\lambda} = \frac{D_0}{\alpha(\overline{A})} \qquad (17)$$

The coefficient s is an averaged product of two factors:

$$s = \frac{1}{d}\int_0^d \exp\left\{\frac{U(x) - U(0)}{kT}\right\} \frac{D_0}{D(x)} dx . \qquad (18)$$

If the surface potential is monotonic, then $U(x) < U(0)$, and the exponential factor is smaller than one. On the other hand the surface order should decrease the diffusion and $D(x) < D_0$. Therefore s is usually about one, but for a non-monotonic potential it can reach 10-10^2.

If the adhesion coefficient (the ratio between the adsorption rate and the number of molecules reached the substrate per unit time) is not very small, then the characteristic length $\bar{\lambda} \le d << L$. However, the adsorption site is occupied by a host LC molecule, and dye molecule adsorption requires the removal of that LC molecule. This apparently barrier-type substitution of a LC molecule with a dye molecule should significantly decrease $\alpha(\bar{A})$ and increase $\bar{\lambda}$. Thus $\bar{\lambda}$ may be larger than d or even larger than L, dominating in the numerator of the fraction in (17).

The Boltzmann factor w of the surface potential for a dye molecule seems to provide the main contribution to the inequality (17). The Van-der-Waals and multipole electrostatic interactions with substrate are different for LC and dye molecules. This difference produces a significant contribution to the surface potential for a dye molecule, that can achieve several kT[7]. In a LC phase, an additional contribution of the surface potential appears due to the intermolecular interaction between LC and dye molecules. Usually, the anisotropic interaction between LC molecules is stronger than with dopants (in our case dye molecules serve as dopants) and the system tries to expel dye molecules from regions with larger orientational and translational order parameters. Estimates for the surface layer in the framework of the Maier-Saupe potential[8] show, that this contribution of the surface potential for a dye molecule can also achieve several kT.

Thus, the surface potential for a dye molecule and barrier-type substitution of a LC molecule and a dye molecule on the substrate cause slow dye adsorption. As we show below, the same factors are responsible for the sensitivity of adsorption to light irradiation.

Light induced adsorption.

Light irradiation from one side breaks the symmetry, because the transmittance of LC cell with dye is much smaller than one and light induced effect is negligible on the backward substrate. Light absorption by dye molecules may affect the adsorption during the non-radiative relaxation of the electronic excitation of a dye molecule through the following mechanisms:

(1) modifying of the surface order and surface potential;
(2) stimulation of substitution processes in adsorption sites (this process could especially effective for light absorption by dye molecules in adsorption layer);
(3) transformation of a dye molecule into another conformation state (for example, trans-cis transformation) with different parameters.

Despite the fact, that all these mechanisms are effective only in the neighborhood of the absorbing dye molecule and induce strictly speaking in-plane inhomogeneities, we suppose, it is acceptable to take them into account by phenomenological change of the model parameters.

The change of $U(0)$ is probably the most important light-induced effect. Decrease of $U(0)$ by several kT increases w more than ten times and therefore results in drastical changes of $\overline{A}_{1,2}$ and $\tau_{1,2}$. The adsorption and desorption coefficients are also rather sensitive to the irradiation because these processes relate to a barrier penetration for dye molecules.

Strong enhancement of the processes near the irradiated substrate allows us to simplify the description of the light-induced effects. Let A_0 be the surface density of adsorbed dyes on the each substrate at the moment $t = t_0$, when irradiation starts. Because of $g_1 << g_2$ under irradiation the surface density of the adsorbed dyes on the backward substrate remains almost unchanged $A_2 \approx A_0$, whereas A_1 on the forward substrate quickly relaxes to the quasi-stationary value $\overline{A}_1$

$$A_1 = A_0 + \left(\overline{A}_1^* - A_0\right)\left(1 - \exp\{-(t - t_0)/\tau_1\}\right) \qquad (19)$$

where $\overline{A}_1^*$ satisfies the equation $\Sigma - A_0 - \overline{A}_1^* - L\overline{C}_1^* = 0$, and the relaxation time τ_1 is significantly smaller than τ_+:

$$\tau_1 = \tau_D \frac{\overline{g}_1 + 1/3}{1 + L\overline{C}_1'}. \qquad (20)$$

After this quick relaxation the surface densities of the adsorbed dyes on **both** substrates are controlled by the slow relaxation with $\tau_2 >> \tau_1$. Figure 2 shows typical kinetics of the surface densities of adsorbed dyes. It is convenient to calculate the surface density in numbers of molecular layers, because in this case σ and h is about one, and Σ is equal to the maximum number of adsorbed layers. The difference in results for calculations with Eq. (6) and Eq.(9) is not distiguishible (solid curves).

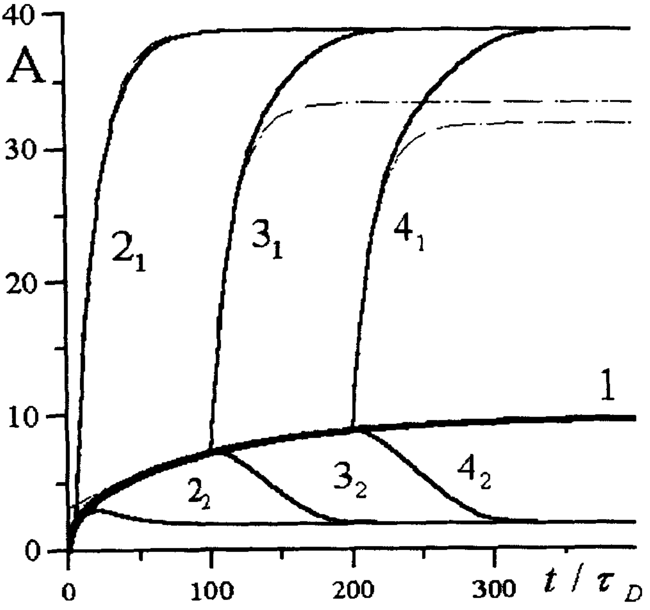

FIGURE 2. Kinetics of the surface densities of adsorbed dyes (in numbers of molecular layers) on the substrates without irradiation (line 1) and with irradiation starting at different moments: (2) $t_0 = 5\tau_D$; (3) $t_0 = 100\tau_D$; (4) $t_0 = 200\tau_D$ (indexes correspond to the substrates). Calculations with Eq. (6) and Eq.(9) give the same results (solid lines). Dashed lines represent linear approximations without (Eq.15) and with (Eq.19) irradiation. Parameters for calculation without irradiation: $\frac{U(0)}{kT} = 6$, $\frac{\beta_\infty}{\alpha_\infty p_0} = 0.2$, $\frac{D_0}{\alpha_\infty L} = 0.5$, $\sigma = 1$, $h = 1$, $d/L = 0.01$, $\alpha_\infty/\alpha_0 = 0.5$, $\Sigma = 100$. Irradiation changes the following parameters for the forward substrate: $\frac{U(0)}{kT} = 5$, $\frac{\beta_\infty}{\alpha_\infty p_0} = 0.4$, $\frac{D_0}{\alpha_\infty L} = 0.1$.

For the dark adsorption, the linear approximation (15) is satisfactory, except in the early stage, when $A<\bar{A}/2$. On the contrary, the linear approximation (19) for light-induced adsorption describes well the early stage of irradiation. During this stage the quick relaxation is dominating and the change of surface density on the backward substrate remains negligible. However, (19) does not take into account complete slow relaxation with the backward substrate and provides the wrong stationary values (curves 3 and 4). Only if irradiation starts when $A_0=\bar{A}_2$, the approximate solution (19) and the exact solution of Eq.(9) almost coincide (curve 2_I).

It should be noted that the model has been developed for an in-plane homogeneous sample, whereas in the experiment a sample is usually irradiated by a laser beam with a finite radius R. Therefore, the description of the light-induced effects is valid for $t \leq R^2/D_0$, otherwise in-plane dye diffusion should be taken into account.

CONCLUSIONS

The proposed model is a suitable basis for analysis of the adsorption processes in LC cells. The slow dye adsorption, caused by the surface potential barrier and by the slow substitution processes in adsorption sites on the substrates, allows one to treat the bulk region as a distributed dye source and to reduce the diffusion equation into the kinetic equations (9) for the surface densities of adsorbed dyes. The solutions of Eq.(9), obtained under various conditions, show that the stationary values and kinetics of dye adsorption in LC cells are determined mainly by the surface parameters: surface potential for dye molecules, adsorption and desorption coefficients. Thus, the dye adsorption strongly depends on the polar orientation of the director on the surface.

The crucial role of the surface region and the large rotational diffusion of the dye molecules allows us to assume, that light-induced effects in the azimuthal orientation are caused by light absorption of molecules, which have already been adsorbed on the substrate or are very close to the substrate. Light absorption by adsorbed dye molecules increases desorption from the substrate. Absorption by molecules in the thin layer S_I reduces the surface barrier and increases the adsorption process. Both effects contribute to the light-induced alignment but with opposite signs, because the dye molecules, participating in light-induced adsorption and desorption processes are predominantly oriented along the light polarization. The light-induced adsorption and desorption effects possibly have different dependencies on the irradiation intensity, so the competition between them can originate the sign change of the light-induced alignment, observed in [9].

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