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Dye adsorption alteration of anchoring properties of planar orienting films

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Planar orienting polymeric films proved to have strong anchoring properties for nematic liquid crystals. Inserting a small quantity of azo-dye in a nematic liquid crystal 5CB changes the anchoring properties due to specific adsorption mechanisms. Measurements have been performed choosing several dye concentrations, cell thicknesses and different dyes. Anchoring strength dependence on the cell thickness has been investigated.

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Keywords: Nematic liquid crystal, Azo-dye, Saturation voltage, Unified anchoring strength

1. Introduction

Recent researches have shown that many scientifically and theoretically interesting phenomena can be successfully manage only by taking into account the intimate mechanisms of interactions between liquid crystal molecules, on one hand, polymer thin films or dye molecules orienting liquid crystals, on the other hand. Liquid crystal electro-optic devices need an aligning film with anisotropic surface anchoring properties [1,2]. To obtain these properties the methods used until 1990's (i.e. oblique evaporated SiO_x, films, thermally treated and rubbed polymeric thin film) presented the shortcomings of physical defects and non uniformities, the generation of dust particles electrically charged or not, etc. A new technique was developed in the nineties, called photoalignment that permitted the alignment and subsequent realignment of the director of a cell already filled with liquid crystal [3], [4]. The photopolymerization technique is a non-contact method that does not induce a mechanical stress on the polymeric surface. In the same nineties people tried to orient the liquid crystal acting not only on the surface of the cell but also on the bulk of LC. It was found that the presence of a small quantity of absorbent dye (less that 1% wt.) dissolved in a nematic liquid crystal (NLC) greatly amplified the orientational response of the liquid crystal. The reorientation effect is generated by the appearance of a supplementary torque, called dye induced torque or absorption induced torque, which proved to be several orders of magnitude greater than the optical one. The dyes are azo- or anthraquinone-derivates with great photostability. The azo dyes have one or more azoic moieties (-N=N-) and have two stable configurations: the trans form and the cis form. Within the limit of small concentrations and small light intensity the two isomers act as independent dopants that give independent contributions to the induced absorbtion torque. Under linear polarized laser light a molecular reorientation is observed in dye doped liquid crystals.

The anchoring energy is a key parameter for the design of the liquid crystal alignment process and materials. It is experimentally known that a nematic liquid crystal (NLC) in contact with a solid surface tends to be oriented in a well defined manner, dependent on the orienting considered surface. In the absence of bulk constraints, this direction is called the easy axis. When a deformation is imposed, for instance, by means of an external field, the surface orientation of the NLC may change or not. In the first case, the anchoring is called weak, in the second case, strong [5], [6]. The most important case for the applications is the weak anchoring case because the threshold fields necessary to induce a deformation in special geometries are a decreasing function of anchoring energy [7]. Various methods for evaluation the anchoring energy have been investigated. There are two type of anchoring energy for NLC: polar and azimuthal anchoring energies [8], [9]. All these methods assume that the easy axes of the two substrates form certain angles, such 0^0 or 90^0. For these measurements, it is very important to determine the alignment treatment directions of substrates, and it is very difficult to do so precisely. An improved method for measuring the azimuthal anchoring energy, using two different chiral dopant cells was proposed by Saitoh and all [10].

On the basis of a general Rapini and Papoular model [11] a unified surface anchoring energy has been proposed to study the director deformation of a twisted chiral nematic sample theoretically [12]. In this model, the surface anchoring energy is generalized to describe an interfacial energy, in which the surface anchoring energy is not separated into polar and azimuthal surface anchoring energies.

The aim of this article is to investigate the anchoring properties of the planar oriented nematic liquid crystal when a small quantity of azo-dye is present. The unified surface- anchoring energy was determined using the saturated voltage method [13]. The anchoring strength

dependence on the cell thickness and concentration of the dye in NLC has been investigated.

2. Experiment

A new saturation voltage method for determining the unified surface anchoring energy at the interface of a NLC (5CB) and its alignment layer (polyvinyl cinamate) has been reported [13].

We will use this method to evaluate the anchoring strength in the azo - dye doped NLC samples. The mixture of NLC with dye is confined between two glass plates assuming that the easy direction and surface anchoring strength at the both substrate are the same. The relationship between the anchoring strength, *A,* and the saturation voltage, U_S, was derivate. [See Eq.56 in Ref.12]

$$\frac{\pi K_{22} K_{33}}{A d K_{11}} = \frac{\tanh(\pi Y/2)}{Y}\left[1+\frac{\cos^2(T)}{\sinh\ (\pi Y/2)}\right], \quad (1)$$

where

$$Y = \sqrt{\frac{U_s^2 \varepsilon_0 \Delta\varepsilon}{\pi^2 K_{33}} - \left(\frac{2dK_{22}}{p_0 K_{33}}\right)}, \quad (2)$$

$$T = \frac{\phi_t}{2} - \frac{\pi d K_{22}}{p_0 K_{33}}\ . \quad (3)$$

K_{11}, K_{22}, K_{33}, are the splay, twist and bend elastic constants of the NLC, respectively, p_0 denotes the pitch of the material induced by a chiral dopant, ϕ_t is the twist angle, $\Delta\varepsilon$ is the dielectric anisotropy, ε_0 is dielectric constant of the material and *d* is the sample thickness.

Using Eqs.(1)-(3) a rigorous relationship between *A* and U_S is obtained:

$$A = \frac{U_s K_{22}\sqrt{\varepsilon_0 \Delta\varepsilon K_{33}}}{d K_{11}} \tanh\left(\frac{U_s}{2}\sqrt{\frac{\varepsilon_0\Delta\varepsilon}{K_{33}}}\right). \quad (4)$$

Consequently, the unified surface anchoring energy, *A*, can be completely determined by measuring the saturated voltage U_S. The estimation of the U_S is made by using a method of determination the optical angle retardation in the NLC doped with azo-dye.

In this study we used nematic liquid crystal 4-pentyl - 4'-cyanobiphenyl known as 5CB (the isotropic phase appear at 35.5^{0}C). (See Fig.1)

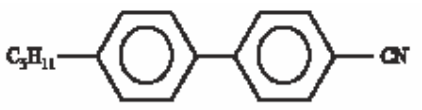

Fig.1. The structure of the 5CB.

The 5CB was mixed with different concentrations of azo-dye (MR, D13, and DO25). The structural formulas of these dyes are shown in Fig.2.

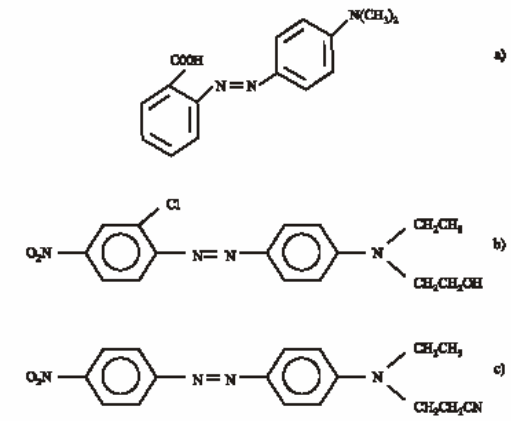

Fig. 2. The structure of the azo dyes: a) Metil Red (MR); b) Dispers Red (DR13); c) Dispers Orange 25 (DO25).

Experiments were carried out using sandwich cells separated by two Mylar spacers of different thickness (*8μm*, *19μm*, and *23μm*). The inner surfaces of the glass plates (both coated with a conductive layer, ITO) are previously cover with a polymer layer by spin coating method. The monomer, polyvinyl alcohol (PVA) was dissolved in H_2O at a concentration of 3% wt. The PVA solution was spin coating on the plates, then baked at 120^{0}C for 60 minutes and cool its down at room temperature.

The substrate surfaces were mechanically rubbed to get a weak planar anchoring. The cells were then filled by capillarity with the mixture of NLC with azo-dye in the isotropic phase (up to 35^{0}C). The inner rubbed surface of the cell imposed a planar alignment through the whole cell.

The experimental set-up is schematically shown in Fig. 3.

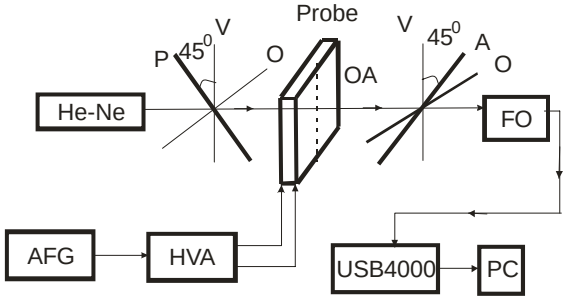

Fig. 3. The experimental set-up. He-He laser, P-Polarizor, A-Analizor, OA-Optical Axis, V-Vertical axis, O-Horizontal axis, FO-Fiber Optic, AFG – Arbitrary High Voltage Amplifier, HVA – High Voltage Amplifier, USB 4000 – Fiber Optic Spectrometer, PC – Personal Computer.

The He-Ne laser (λ=*633 nm*) has the power P_{test}=*2 mW*, the divergence equal with *1.2 mrad*. The polarization of the laser beam is 1000:1 for the vertical electric component. The polarizer, P, and the analyzer, A, were set at an angle of 45^0 with respect to the He-Ne laser beam polarization direction and make an angle of 90^0 between them.

The sample (cell) is positioned with the nematic director (the direction of the optical axes, OA) parallel to the He-Ne beam polarization direction which corresponds to a minimum of the transmitted light.

An alternative electric voltage (a wave form type "ramp up") with a period of *100 s* and amplitude from zero to *100 V* peak to peak was applied across the cell using a Tektronix - Arbitrary Function Generator (AFG) and a High Voltage Amplifier- TEGAM

The beam intensity measurement of the light throughout the cell was performed by a optical fiber (OF) connected with a Fiber Optic Spectrometer, Ocean Optics USB4000 and a computer (PC).

The intensity of the transmitted laser beam in the direction perpendicular to the initial nematic director as a function of the applied electric voltage have been measured.

3. Experimental results

The dependence of the transmitted light in the cell for three periods (*T=100 s*) of applied electric voltage is presented in Fig. 4. The waveform of the electric voltage is also presented in Fig. 4. The waveform of the electric voltage is "ramp up" with the amplitude varying from *0* to *50 V*. The cell (thickness of *8*μm) was filled with 5CB doped with 1.5% MR.

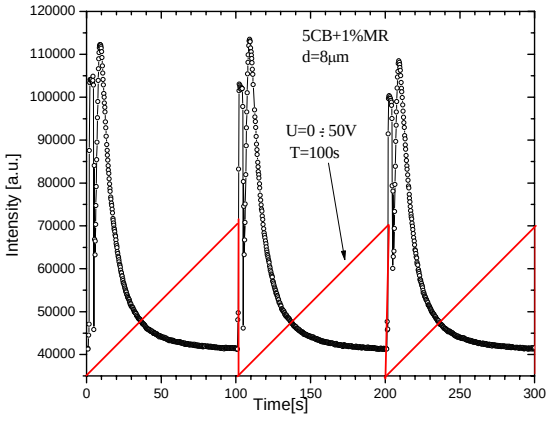

Fig. 4. The dependence of the intensity of laser beam for three periods of electric voltage. The waveform of electric is "rump up" with the amplitude voltage from 0 to 50 V.

When an external field is applied the nematic director tends to align parallel to the direction of the electric field. In our experiment the direction of the external field is perpendicular on the limiting surfaces of the cell. Due to the variation of the effective refractive index in the dye doped nematic cell the transmitted light presents interference fringes.

The last maxim of the light transmittance corresponds to an optical retardation equal to π and it is followed by a transmittance decay through a minimum value at the large amplitude of electric voltage. In this situation the orientation of the cell becomes practically homeotropic with minimum of the transmittance through the cross polarizers.

The intensity of the transmitted He-Ne laser beam as function of the amplitude of the electric voltage is presented for the cells containing 5CB doped with 2% MR, 2% DR13 and 2% DO25, with the same thickness (*d=23*μm) in Fig.5-7.

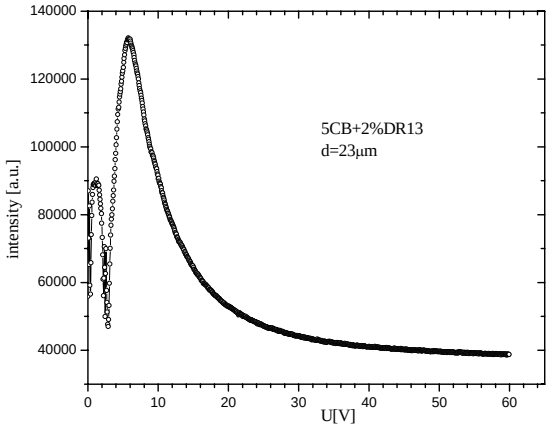

Fig. 5. The dependence of the intensity of laser beam versus amplitude of the electric voltage (5CB with 2% DR 13; d=23 μm.

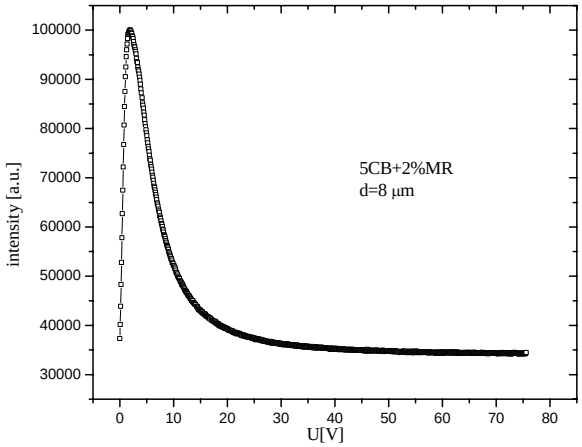

Fig. 6. The dependence of the intensity of laser beam versus amplitude of the electric voltage (5CB with 2% MR; d = 8 μm).

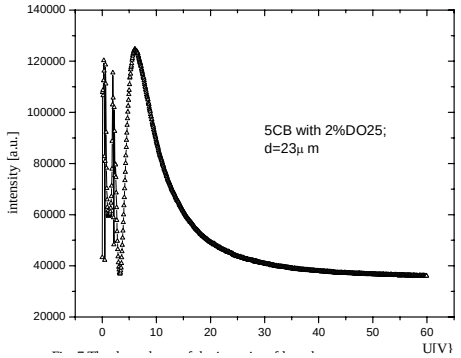

Fig. 6. The dependence of the intensity of laser beam versus amplitude of the electric voltage (5CB with 2% DO25; d=23 μm).

4. Optical Retardation. Estimation of the Unified Anchoring Energy

When an external field is applied to the liquid crystalline sample, the orientation of the director *n* became parallel to the electric field. The interference fringes shown in the Figs. 5-7 can be explain by considering the variation of the effective refractive index with the polar angle, ϕ, which is the angle between the direction of the applied electric field and the normal to the limiting surfaces of the cell:

$$\frac{1}{n_{ef}^2} = \frac{\cos^2\phi}{n_0^2} + \frac{\sin^2\phi}{n_e^2}, \tag{5}$$

where n_0 and n_e are ordinary and extraordinary refractive indices. We remark that in the high voltage regime, the intensity tends to zero, which means that the LC tends to became homeotropic. The saturation voltage is the value of applied voltage for which entire nematic liquid crystal cell (including the boundary layers) is oriented along the external field direction. As the values of the saturation voltage U_S can be rather large, sometimes it can not be directly measured because of the possibility of the sample damage. We estimate the saturation voltage from the extrapolation of the calculated optical retardation versus the inverse of the applied voltage.

The intensity of the transmitted laser light through the analyzer I_{tr} can be calculated by the following formula:

$$I_{tr} = I_0 \sin^2(\Delta\varphi/2), \tag{6}$$

where:

$$\Delta\varphi = 2\pi\Delta n_{eff}(\lambda)d/\lambda, \tag{7}$$

is the optical retardation of a liquid crystal slab, $\Delta n_{eff}(\lambda)$ is the effective optical birefringence of a dye doped NLC, *d* is the thickness of the probe, $\lambda=633nm$ is the wave length of He-Ne laser. From the relations (6) and (7) we obtain immediately:

$$\sin^2(\Delta\varphi/2) = \frac{I_{tr}}{I_0}, \tag{8}$$

and, with the "dark" correction (8) becomes

$$\sin^2(\Delta\varphi/2) = \frac{I_{tr} - I_{dark}}{I_0 - I_{dark}}. \tag{9}$$

Finally:

$$\Delta\varphi = 2\arcsin\sqrt{\frac{I_{tr} - I_{dark}}{I_0 - I_{dark}}}. \tag{10}$$

The optical retardation introduced by the probe, $\Delta\varphi$, depends on the optical path difference $\delta=\Delta n_{eff}(\lambda)d$. In the high voltage regime, δ is inversely proportional to the applied voltage U [13], so we can consider a dependence of this form:

$$\delta = F + \frac{B}{U} + \frac{C}{U^2} + \frac{D}{U^3} + \dots . \tag{11}$$

Eqs. (7), (10), (11) give the relation:

$$\arcsin\sqrt{\frac{I_{tr} - I_{dark}}{I_0 - I_{dark}}} = F' + \frac{B'}{U} + \frac{C'}{U^2} + \frac{D'}{U^3} + \dots, \tag{12}$$

where, we note:

$$F' = \frac{\pi A}{\lambda}, B' = \frac{\pi B}{\lambda}, C' = \frac{\pi C}{\lambda}, D' = \frac{\pi D}{\lambda} + \dots . \tag{13}$$

The real solution (and physically accepted) of the best polynomial fit, for the values of optical retardation as a function of U^{-1}, represents the saturation voltage, U_S (See Fig.8-10). We present below the plots of the polynomial functions, and the value of U_S .

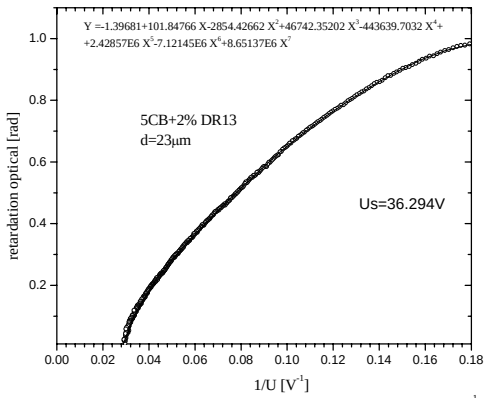

Fig. 8. The dependence of the optical retardation, Δφ versus 1/U [V^{-1}].

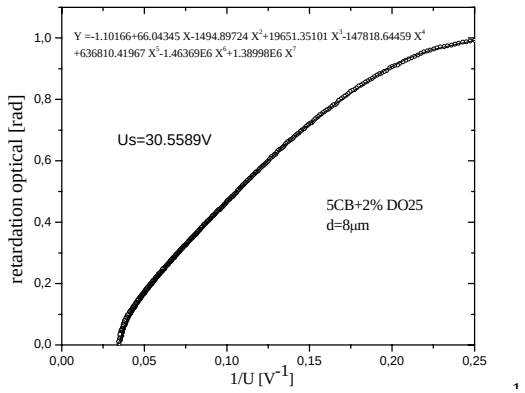

Fig. 9. The dependence of the optical retardation, Δφ versus 1/U [V^{-1}].

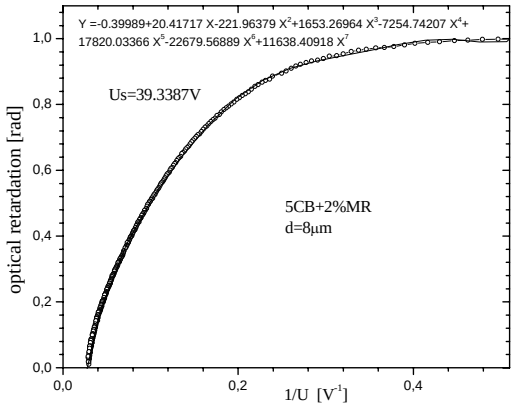

Fig. 10. The dependence of the optical retardation, Δφ versus 1/U [V^{-1}].

We determine the values of unified anchoring energy, A, substituting U_S into Eq.(4). From the definition of saturation transition, the values of U_S can be determined for zero optical retardation and the unified anchoring energy can be estimated from Eq.(4). Because

$$U_s > 2\sqrt{\frac{k_{33}}{\varepsilon_0 \Delta\varepsilon}}$$

is the most common case, a simpler formula for A is used :

$$A = \frac{U_S k_{22}\sqrt{\varepsilon_0 \Delta\varepsilon k_{33}}}{d k_{11}} \qquad (14)$$

where the values of the constants for 5CB at 299K mentioned in literature [13]:

$$k_{11} = 7.0\times10^{-12}\,N, k_{22} = 3.9\times10^{-12}\,N,$$
$$k_{33} = 8.4\times10^{-12}\,N, \Delta\varepsilon = 10$$

Table 1.

Probe	d [μm]	U_S [V]	A 10^{-5} x [J/m^2]
1.5%MR+5CB	8	32.63	6.158
1.5%MR+5CB	19	44.33	3.520
1.5%MR+5CB	23	46.25	3.168

We remark a dependence of the unified anchoring energy, A, on the thickness d of the probes of 1.5% MR doped 5CB [see Table 1]. This dependence is not reported for the pure NLC probe [14]. For comparison, we report that, for 5CB pure probe with $d=23\mu m$, we obtained the saturation voltage $U_S = 50V$ and the unified anchoring energy, $A=3.282\ 10^{-5}\ J/m^2$ in the same experimental conditions. The adsorbtion of the dye molecules on the two limiting surfaces could be responsible for the anchoring energy dependence on the cell thickness.

The unified anchoring energy of the NLC molecules decreases because the dye molecules are adsorbed on the orienting substrate, in comparison with situation when the NLC molecules are in direct contact with polymeric substrate for the same thickness of the probe. The presence of the dye molecules acts like defects on the aligning substrate and determines a decrease of anchoring strength when increasing the thickness of the cell (which means that more dye molecules will be "attached" on the surface).

The same considerations are valid to explain the dependence of unified anchoring energy with the concentration of azo-dye molecules in NLC cells when the d was maintained constant. [See Table 2] .

Table 2.

Probe	d [μm]	U_S [V]	A 10^{-5} x [J/m^2]
1% MR+5CB	8	32.27	6.01
1.5%MR+5CB	8	32.63	6.158
2% MR+5CB	8	39.33	7.423

Table 3.

Probe	d [μm]	U_S [V]	A 10^{-5} x [J/m^2]
2%DR13+5CB	8	24.02	4.533
2%DR13+5CB	23	36.29	2.382
2%DO25+5CB	8	30.55	5.766
2%DO25+5CB	23	45.11	2.961

The unified anchoring energy and the saturation voltage for different azo-dye doped NLC cells are shown in Table 3.

In the adsorption process, the molecules go to surface substrate and remain attach on it. In general, the adsorption phenomenon happens due to the electro-chemical interaction between the particles of system and a surface and is present in many situations (such as, the adsorption of the perfect gas molecules or a charge molecules from an electrolyte).

In our case, since this process is generated in a macroscopic system, at constant temperature, it can be described using thermodynamic models. The Maxwell-Boltzmann theory can be directly applied only in the case of diluted systems. A phenomenological model based on the equilibrium properties of neutral molecules adsorbed onto two identical parallel surfaces is under development.

5. Conclusions

As it is known, the anchoring energy for the pure NLC doesn't depend of the thickness of the probe [14]. Despite this, in our experimental measurements with symmetric nematic cells doped with different azo-dye molecules a dependence of the unified anchoring energy, *A*, on the thickness of cell, *d*, has been observed. A dependence of the unified anchoring energy with the concentration of azo-dye in NLC for the same thickness was also obtained.

The variation of the anchoring energy with the thickness of the probe could be explained by the adsorption of dye molecules on the aligning surface. The dye molecules adsorbed on the surfaces modify the interaction at the interfaces and obviously the anchoring strength of the liquid crystals at the substrates.

The explanation of the adsorption process of dye molecules on the polymeric substrate and the influence of this phenomenon on the anchoring strength is our goal for next studies.

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