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Electrically Induced Bleaching of Ion-dye Doped Nematic Liquid Crystal

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We report on electrically controlled chromatic effect in liquid crystals (LC) doped with ion-dye astrofloxine molecules. We investigated the dependencies of visible spectra of the system on concentration, electric field and time of applying of *dc*-field. We also measured conductivity of the system on the cell age. Obtained results allowed us to associate the photochromic effect with neutralizing of the ion-dye molecules on the aligning surfaces. The application of the *dc*-field causes spatial separation of the charges in the cell and their adsorption on the aligning surfaces. The adsorption results in a sharp decrease of the electron conjugation in the dye molecules and in turn, to the bleaching effect.

Keyword: liquid crystal; adsorption; desorption, ion-dye.

INTRODUCTION

Electrically controlled chromatic effect (bleaching of liquid crystal cell caused by electric field) is known for dye doped liquid crystals[1]. It has not been investigated in depth although it is very promising due to possibility of using it in electrically controlled devices of optical storage and processing. Nazarenko *et al*[1] shown that the effect is uniquely strong for nematic 5CB doped with ion dye astrofloxine (Fig. 1). The authors related the bleaching of the system with presence of *J*-aggregates of astrofloxine that are ruined by the electric field.

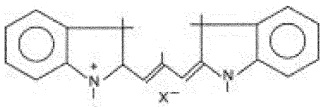

FIGURE 1. Chemical formula of astrofloxine

The aim of our work was to study and identify the origin of this effect.

BASIC EXPERIMENTS

We studied a bleaching of mixture of ion-dye and 5CB in the cell made from two glass substrates, which inner surfaces were covered with ITO electrodes cell. Thickness of the cells, 60 μm, was given by calibrated spacers. The dye concentration varied from 0.01% to 0.1% by weight. Measurements were carried out with the room temperature with LC being in nematic phase. The cells were irradiated by light from wolfram lamp with the power about 0.1 mWt/cm^2 in the plane of the sample.

The typical dependence of optical density of our system at wavelength that corresponds to the best absorption of the dye (ë = 560 nm) on time of applying of *dc*-field is presented on Fig. 2. The kinetics of the bleaching was poorly reproducible in the nematic phase; despite of the same characteristic time of the process (~ 200 s) the shape of the kinetics curve changed from the measurement to the measurement.

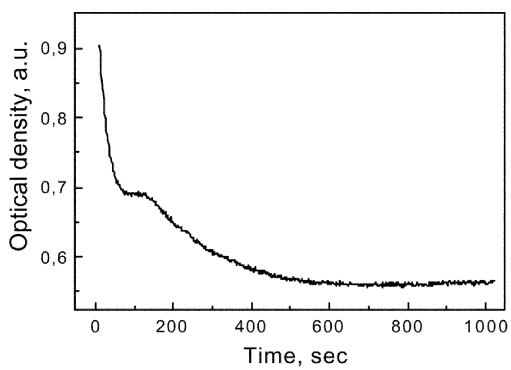

FIGURE 2. Kinetics of bleaching of 5CB doped with astrofloxine (c = 0.05%), *dc*-field voltage is 20 V, T = 20°C.

The same experiments carried out at temperature 50°C when LC is in isotropic phase (Fig. 3) gave smooth kinetics curve with two characteristic times: the first one is about 20 s, and the second one is much larger (>100 s). The results in the isotropic phase were well reproducible. The difference in the kinetics curves in the nematic and isotropic phase points an important role of the orientational molecular ordering in the bleaching of the nematic phase.

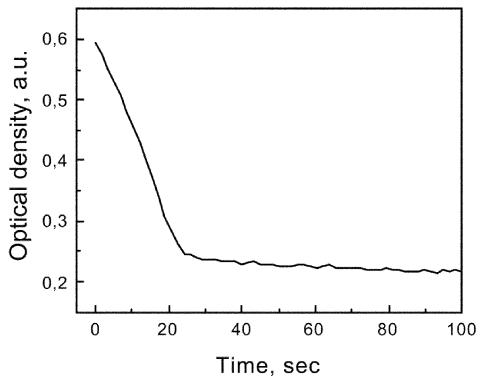

FIGURE 3. Kinetics of bleaching of 5CB doped with astrofloxine (c = 0.05%), *dc*-field voltage is 20 V, T=50°C (LC is in isotropic phase)

After the bleaching, the cells slowly relaxed to their initial state within a week.

The bleaching was observed in the whole range of the absorption band of the dye. In figure 4 one can see the "astrofloxine-5CB" spectra, measured right after application of the voltage U = 20 V during 30 s at different frequency. It is seen that *dc*-field causes strong decrease of spectra intensity and increase of the cell transmittance. There was no effect observed for *ac*-field.

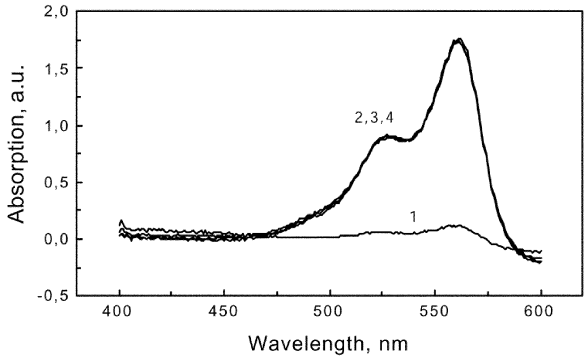

FIGURE 4. Absorption spectra of "Astroflixine-5CB" system after applying of electric field: *dc*-field (1), 100 Hz (2), 1000 Hz (3), 5000 Hz (4).

Application of the electric field changed drastically not only optical but also electrical characteristics of the dye-doped 5CB. We measured the conductivity of the cell depending on the time since the cell was filled. It is seen (Fig. 5) that conductivity of the cell decreases fast during first several minutes after the filling followed by slower decrease of the conductivity taking place during tenth of hours. The following application of *dc*-field (20 *V*, 30 s) resulted in additional several times decrease of the conductivity.

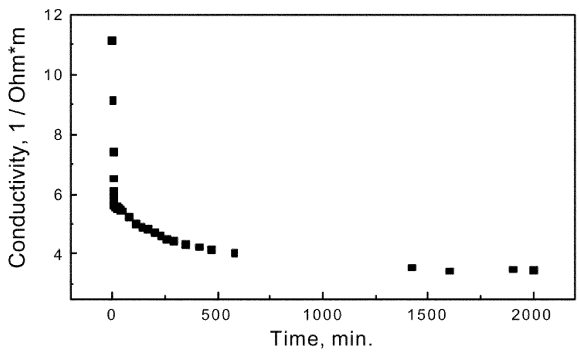

FIGURE 5. Cell conductivity depending on cell lifetime

ADDITIONAL EXPERIMENTS AND DISCUSSION

Our data on the electrically induced changes of spectra of dye-doped LC qualitatively coincide with results of Nazarenko *et al*. and could be explained by the *J*-aggregates model. At the same time, changing of cell's conductivity indicate that effect can be strongly connected to the processes of interaction of dye ions and surface of ITO. Indeed, decreasing of conductivity usually associated with adsorption of dye molecules on the surface. To find out the origin of the effect, we carried out additional experiments.

The model of *J*-aggregates assumes dramatic changes in spectra after applying of the field. At the same time we did not find any changes in these spectra, only general decrease of the absorption. Moreover, the spectra in 5CB are similar to those in toluene and dioxane, where there are definitely no *J*-aggregates[2] (Fig. 6).

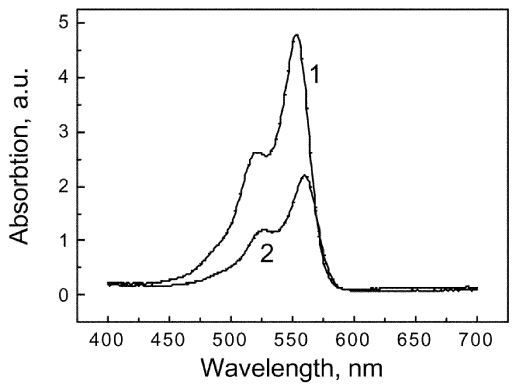

FIGURE 6. Spectra of astrofloxine dissolved in dioxane (1) and toluene (2)

It is well known that formation of *J*-aggregates with the increase of the dye concentration is accompanied by appearance of a sharp absorption band on the red wing of the monomer absorption[3]. At the same time we did not find such behavior in our case (Fig. 7). All this allows us to suggest the absence of *J*-aggregates in our system and consider the *J*-aggregates model very doubtful.

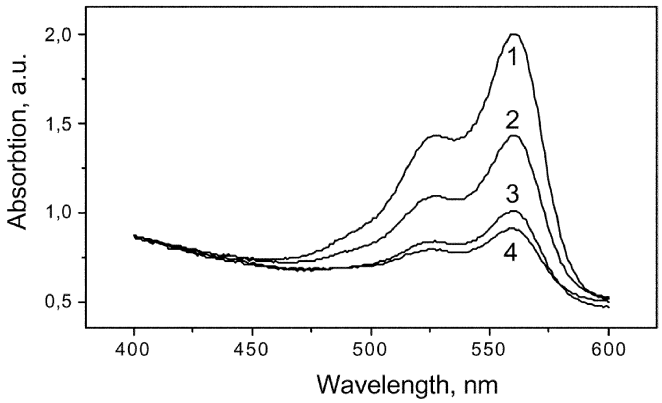

FIGURE 7. Spectra of 5CB doped with astrofloxine (1 – 0.1%, 2 – 0.05%, 3 – 0.025%, 4 – 0.01%)

To check our suggestion about the "surface" origin of the effect, we carried out the following experiment. We pre-bleached the cell by application of *dc*-field during 15 s so that the cell did not bleach completely, being light-red colored. Afterwards, we split the cell apart. We found that negative electrode was light-red colored, and the positive one was transparent. This fact testifies that positive dye ions are adsorbed by the surface.

The last experiment clearly points a surface origin of the effect and allows us to propose the next mechanism of the bleaching. Application of *dc*-field causes positively charged ions of astrofloxine, (responsible for light absorption) to adsorb on negatively charged surface (Fig. 8). They adsorbed and chemically react with and I^+ ions that ever present on ITO surfaces. This reaction results in bleaching of dyes of this type due to the break of chromofore group[4] that explain electrically induced transparency of our system. As the 5CB and astrofloxine is electrolyte, its conductivity depends on number of charge carriers. With adsorption of ions this number decreases that leads to the observed decrease of the conductivity after application of *dc*-field. A dark adsorption of the dye molecules on the ITO surface after the cell filling causes a slow decrease of the cell conductivity during first hours of the cell age.

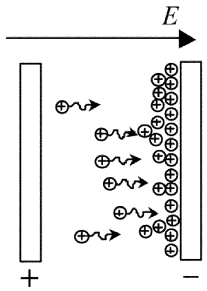

FIGURE 8. Scenario of the effect (for the simplicity, only positive ions are depicted)

CONCLUSIONS

Thus, studying the action of electric field on a cell filled with the mixture of astrofloxine and 5CB proved that electrically induced bleaching of LC cell doped with ion-dye is caused by spatial separation of the charges in the cell and their following adsorption on the aligning surfaces. The adsorption results in a sharp decrease of the electron conjugation in the dye molecules and in turn, to the bleaching effect. We believe that further optimization of parameters of ion-doped LCs will allow to create new perspective electrically controlled optical devices.

Acknowledgement
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