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Spectral Studies of Dimethylaniline Ethylene Ketone Dyes in Ferroelectric Liquid Crystals

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Spectral Studies of Dimethylaniline Ethylene Ketone Dyes in Ferroelectric Liquid Crystals

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We have studied the dependences of the spectra of absorption and photoluminescence of dimethylaniline ethylene ketone (DMAEK) dye dissolved in ferroelectric liquid crystals (FELCs) on the temperature.

We have revealed the significant dependences of the spectra of absorption and luminescence of DMAEK dyes on the phase of the liquid crystal matrix, which testifies to the essential influence of the ordering of the matrix on both the intermolecular interaction of molecules of the dyes and the process of formation of aggregates.

Keywords: aggregation; dimethylaniline ethylene ketone dye; ferroelectric liquid crystal; spectrum of absorption; spectrum of photoluminescence

INTRODUCTION

The interest in liquid crystals (LCs) is caused to a great extent by potentialities of their practical use in various electrooptical devices. Essential limitations on the use of LCs are related to the fact that they have no bands of absorption of the electromagnetic emission in the visual range. One of the ways to improve the characteristics and to extend the regions of practical applications of LC-devices is the introduction of dyes that absorb the electromagnetic emission in the visual range into them. Hence, dyes must be soluble in LC. The studies indicate that DMAEK-dyes possess a sufficient solubility in a number

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of LCs. It is established, in particular, that a solution of DMAEK-dyes in nematic LCs is a material promising for the recording of dynamic holograms in the two- and four-beam geometries [1].

In what follows, we will describe the spectra of absorption and photoluminescence of solutions of these dyes in FELCs. To analyze the spectra of dyes dissolved in FELCs, we compare them with both the spectra of solutions in isotropic solvents described by us earlier in work [2] and the spectra of thin films of DMAEK applied from a solution in dimethylformamide on the plates which are rapidly rotating. The structure of such films is studied with the help of a polarization microscope Olympus (BX51).

EXPERIMENTAL PROCEDURE

The structural formulas of molecules of the DMAEK dyes of orange (K_1) and yellow (K_2) colors are presented in Figure 1. A molecule of dye K_1 contains a carbonyl group $\frac{1}{2}C=O$ at its center, in which positions 1 and 2 can be occupied, respectively, by a radical of methylfuran and dimethylaniline ethylene. In a molecule of dye K_2 , a radical of methylfuran is substituted by methoxybenzene.

The spectra of absorption of the dyes in the wavelength range 250–600 nm are studied with the help of a double-beam spectrophotometer “Hitachi” equipped with a personal computer. In this case, we used standard quartz cuvettes with various thicknesses, which allow us to investigate the dependence of the optical absorption on the concentration of dyes in a solution. As isotropic solvents, we took toluene, dimethylformamide, ethyl alcohol, hexane, and glycerol.

To measure the spectra of luminescence of solutions, we used a computerized spectral set-up on the base of a monochromator SPM-2 with the photoelectric registration of signals. The photoluminescence of the dyes was excited by the emission of a mercury lamp DRSh-250 which was transmits by filters UFS-6 and UFS-8.

FELC, which was used as an anisotropic solvent for studying the influence of an anisotropy of the matrix on the interaction of extrinsic

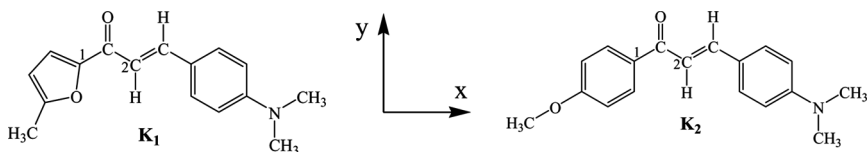


FIGURE 1 Structural formulas of 1-methoxyfuryl,2-dimethylaniline ethylene ketone (K_1) and 1-methoxybenzene,2-dimethylaniline ethylene ketone (K_2).

molecules, is an eutectic mixture of complex ethers 4-n-hexyloxyphenyl-4-n-octyloxybenzoate and 4-n-hexyloxyphenyl-4-n-decyloxybenzoate with chiral admixture Promin-15 [3]. The relative masses of components of the mixture were 31.2; 62.3, and 6.5 mass%, respectively. The diagram of phase states of FELCs and the temperatures (in Kelvin degrees) of phase transitions of FELCs are as follows:



The content of the dyes in FELCs was 1.1–1.2 mass%. In specimens of the “sandwich” type, the restricting surfaces were quartz plates, the distance between which was about 20 μm . We studied both oriented and non-oriented specimens.

On the study of the spectra of absorption of solutions of the dyes in FELC with a double-beam spectrograph, we positioned the pure FELC in the comparison channel for the compensation.

In order to orient FELC, we applied a layer of polyimide on the surface of substrates. This layer was polished with a fabric made of velvet (planar orientation). The specimens without such a processing of the surface of plates were non-oriented. Prior to the filling of specimens by a solution, we measured the distance between plates with the help of the interference method.

The filling by a solution was realized with the help of the capillary forces at temperatures $T > 358^\circ\text{K}$ (isotropic phase of FELC). The temperature was stabilized with an error of at most 0.2 K with the help of a thermostat, whose heating element was a layer of SnO_2 applied on a glass substrate which is transparent in the visual range of wavelengths. This allowed us to decrease (as compared with most of the thermostats which are fabricated by the industry) the size of a thermostat itself and to connect it without any particular difficulties with various optical devices.

EXPERIMENTAL RESULTS

The introduction of an admixture of dyes did not affect the sequence of phases of FELC and did not practically change the temperatures of phase transitions.

In Figure 2, we give the spectra of absorption of solutions of dye K_1 in benzene ($C = 2 \cdot 10^{-5} \text{ M}$, where $\text{M} = \text{mole/l}$) (1), the polycrystalline films of K_1 (2) at a temperature of 293 K, and solutions of K_1 in FELC at various temperatures.

The spectrum of absorption of a solution of K_1 in the Chol-phase of a non-oriented solvent FELC (Fig. 2, curve 3) at a temperature of 352 K

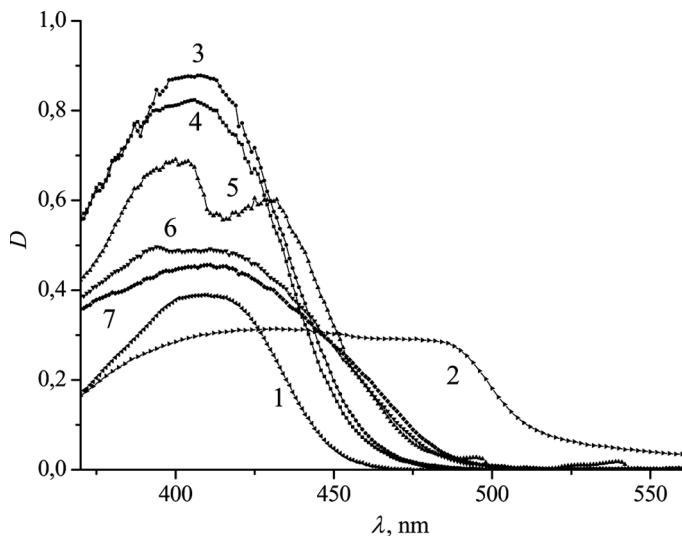


FIGURE 2 Spectra of absorption of the solutions of dye K_1 in benzene (1) and the polycrystalline films of K_1 (2) at a temperature of 293 K, and the solutions of K_1 in FELC at the temperatures $T=352$; 344.8; 334; 329.4, and 317.6 K (curves 3–7, respectively).

has a broad asymmetric band with the maximum of absorption at $\lambda_{\max} = 410$ nm close to its position in the spectrum of the isotropic solvent benzene (curve 1). This band does not vary on the transition of FELC in the SmA-phase at 344.8 K (Fig. 2, curve 4). In the chiral smectic C-phase (SmC*), the band of absorption of dye K_1 at $T = 334$ K is significantly widened due to the increase of the absorption on the long-wave edge. In addition, it is split into two bands with the maxima at $\lambda_{\max} = 393$ and 424 nm (curve 5). A decrease in the temperature in the limits of the smectic C-phase, SmC*, down to 329.4 and 317.6° K (curves 6 and 7, respectively) shifts the positions of the maxima of absorption of K_1 to the short-wave spectral region (hypsochromic effect). The broadening of bands and the presence of the isosbestic point of their intersection can testify to the appearance of an additional band of absorption of K_1 in the interval of wavelengths $\lambda = 450$ –480 nm. We failed to obtain the spectrum of absorption of K_1 in the solid phase of FELC due to the strong scattering of light by the liquid crystal.

The spectrum of absorption of a solid polycrystalline film of K_1 (Fig. 2, curve 2) covers the region from 400 to 500 nm. It is significantly broadened, shifted to the long-wave region (bathochromic effect) relative to the spectrum of absorption of a solution of the dye

in benzene, and characterized by the presence of two components with $\lambda_{\max} = 428$ and 478 nm.

The normalized spectra of photoluminescence of solutions of K_1 in various phases of the non-oriented liquid crystal are shown in Figure 3. In the isotropic phase at $T = 363$ K, a broad asymmetric band of photoluminescence of K_1 at $\lambda_{\max} = 479$ nm (curve 1) is observed. As the temperature of the solution decreases, its maximum bathochromically shifts. In SmA- and SmC*-phases ($345 < T < 349$ and $313 < T < 345$, respectively), its maxima are positioned at $\lambda_{\max} = 491$ and 500 nm (curves 3 and 4, respectively). At room temperature in the solid FELC-matrix, the band of photoluminescence of K_1 is split into two components with $\lambda_{\max} = 484$ and 516 nm (curve 5).

In the spectrum of photoluminescence of polycrystalline films produced by the method of application of the dye solution in dimethylformamide on the plates which are rapidly rotating, we observe a broad asymmetric band which is split into two components with their maxima at $\lambda_{\max} = 543$ and 604 nm (Fig. 3, curve 6).

In the specimens with a planarly oriented FELC (the long axes of LC molecules are mainly aligned in parallel to the substrate), the positions of the bands of photoluminescence do not vary practically as compared with those in non-oriented specimens on the registration of the

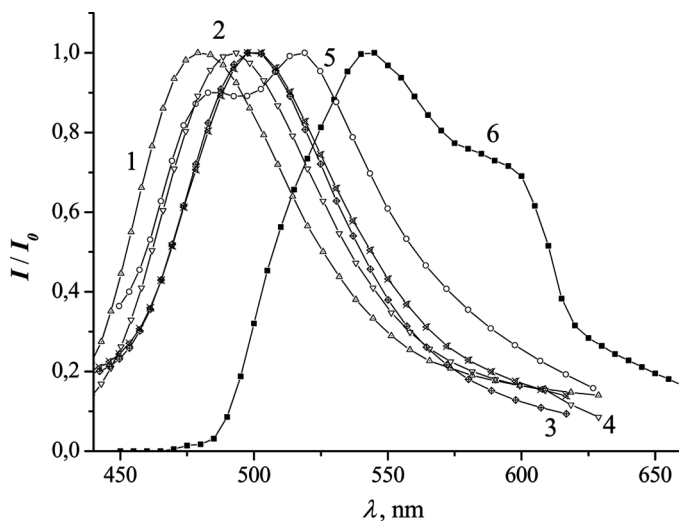


FIGURE 3 Spectra of photoluminescence of the solutions of K_1 in non-oriented FELCs at temperatures of 363, 352, 345, 314, and 293 K which are normalized by the maximum value (curves 1–5, respectively) and a polycrystalline film of K_1 at a temperature of 293 K (6).

spectra of photoluminescence in a polarized light (a polarizer was placed after the specimen in parallel or normally to the LC director orientation direction).

Since molecules of dyes in the oriented FELC are positioned mainly along the orientation axis of molecules of the matrix, they absorb selectively the light with the electric field strength vector \mathbf{E} which is collinear to the orientation axis of molecules of LC. For this reason, the spectra of luminescence of dyes K_1 and K_2 are partially polarized.

The spectra of the polarization of emission $P(\lambda_{\text{exp}})$, i.e., the dependence of the degree of polarization P on the wavelength λ_{exp} at the invariable wavelength of exciting light $\lambda_{\text{exc}} = 365 \text{ nm}$, are presented in Figure 4. The luminescence polarization degree is defined by the formula

$$P = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + I_{\perp}} \quad (2)$$

where I_{\parallel} and I_{\perp} are, respectively, the intensities of luminescence of a dye at the parallel and perpendicular orientations of a polarizer relative to the orientation axis of molecules of FELC.

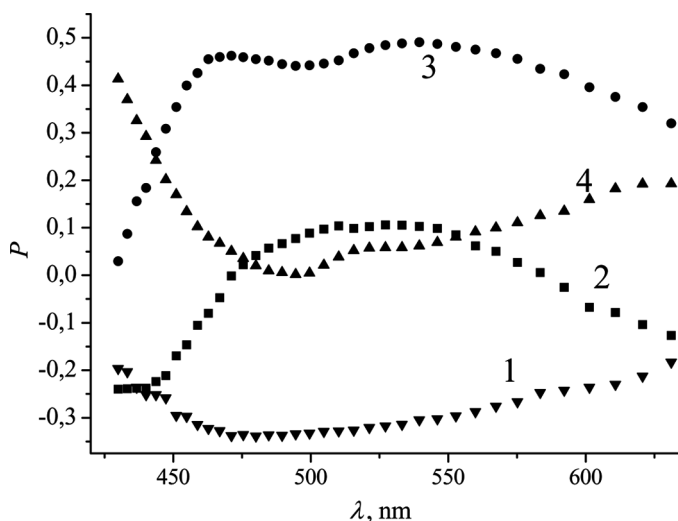


FIGURE 4 Spectra of the polarization of photoluminescence of solutions of dye K_1 in various phases of the FELC matrix: Chol- (1); SmA- (2); SmC*- (3); and solid phase (4).

The luminescence polarization degree depends on the phase of an LC solvent. In the Chol-phase of FELC, $P(\lambda_{\text{exp}})$ decreases firstly down to the least value (-0.32) at the maximum of the photoluminescence of K_1 ($\lambda_{\text{max}} = 504$ nm) with increase in the wavelength of light and then increases gradually to (-0.18) (Fig. 4, curve 1). At $430 < \lambda_{\text{exp}} < 610$ nm, the spectrum of $P(\lambda_{\text{exp}})$ anticorrelates with the spectrum of photoluminescence.

In the SmA-phase, the course of the dependence $P(\lambda_{\text{exp}})$ (Fig. 4, curve 2) is opposite as compared with that for the Chol-phase. $P(\lambda_{\text{exp}})$ changes its sign at $\lambda_{\text{exp}} = 470$ nm and attains the greatest value (0.1) at the maximum of the photoluminescence of the dye ($\lambda_{\text{max}} = 508$ nm); then the values of $P(\lambda_{\text{exp}})$ decrease, by changing their sign at $\lambda_{\text{exp}} = 583$ nm.

In the SmC*-phase, $P(\lambda_{\text{exp}}) > 0$ at $430 < \lambda_{\text{exp}} < 630$ nm and correlates with the spectrum of photoluminescence (Fig. 4, curve 3). At the maximum of the dye luminescence ($\lambda_{\text{max}} = 510$ nm), $P(\lambda_{\text{exp}}) = 0.46$. At $\lambda_{\text{exp}} \geq 550$ nm, we observe a smooth decrease in $P(\lambda_{\text{exp}})$.

In the solid state of FELC, the spectrum $P(\lambda_{\text{exp}})$ anticorrelates with the spectrum of photoluminescence like that in the Chol-phase. At the maxima of the photoluminescence of dye K_1 ($\lambda = 484$ and 524 nm), the values of $P(\lambda_{\text{exp}})$ are minimum and equal, respectively, 0 and 0.05 .

After the long-term irradiation of specimens with UV-light, we observe a decrease in the intensity of photoluminescence proportionally to the irradiation duration. In this case, the bands of luminescence are hypsochromically shifted relative to the bands of nonirradiated specimens. This testifies to the phototransformation of molecules of the dyes; as a result, a part of molecules is nonradiatively deactivated after the excitation or forms nonluminescent associates.

The course of the dependence $P(\lambda_{\text{exp}})$ after the UV-irradiation of specimens was not practically changed as compared with that measured prior to the irradiation. In the SmC*-phase, the maximum value value of $P(\lambda_{\text{exp}})$ increases by 0.1 . In the solid state of FELC, $P(\lambda_{\text{exp}}) = 0.23$ after the irradiation and is independent of the wavelength.

DISCUSSION

The studied dyes belong to unsaturated ketones. Their fragments (between furan and benzene rings in molecules of dye K_1 and between benzene rings in molecules of dye K_2) are planar; therefore, the valence electrons of C and O atoms (carbonyl group) become delocalized with the formation of π -systems of K_1 and K_2 . The atoms O of carbonyl groups form π -bonds by the own $2p_z$ -electrons. The unshared pairs of $2p_x$ -electrons are localized on the nonbonding orbitals.

On the analysis of the spectra of dyes in isotropic solvents [2], it was concluded that $\pi\pi^*$ - and $n\pi^*$ -states are possible in molecules of dyes K_1 and K_2 . The long-wave band of absorption and the corresponding band of photoluminescence of dyes K_1 and K_2 are $\pi\pi^*$ -states and are caused by the excitation of the whole π -system that is composed from valence electrons of carbonyl and ethylene groups, as well as dimethylaniline groups.

On the change in the polarity of a solvent and an increase in the dye concentration, one observes changes in the spectra which are induced by the formation of associates of molecules of the dyes with molecules of a solvent (through hydrogen bonds) and aggregates of molecules of the dyes.

The structure of films of K_1 is polycrystalline (Fig. 5a) and is more clearly manifested in polarized light (Fig. 5b). They are composed from densely packed sphaerolitic crystallites that grow in the radial direction relative to centers of crystallization [4]. The spectra of absorption of polycrystalline films can be explained in the frame of the theory of excitons [5,6]. According to it, the energy of excitonic bands is defined by the excitation energy of isolated molecules, E_0 , a change of the interaction intensity of an excited molecule of the dye with surrounding nonexcited molecules in the crystal D^f , and the resonance interaction parameter β . The comparison of the spectra of polycrystalline films and solutions of the dyes in benzene allows us to estimate the values of D^f and β which are, respectively, -0.275 and -0.155 eV and to conclude that the excited molecules of a dye interact with the environment more intensively than those in the ground state.

In the liquid crystal matrix, we observe both the nonmonotonic dependence of the absorption intensity on the temperature of specimens and the essential differences in the forms of the spectra on the variation of the temperature, which is accompanied by the change of a phase of FELC. The absorption intensity at the maximum increases first under cooling, but then decreases almost twice under the further cooling. In this case, the band becomes significantly broader: a shift of the long-wave edge into the visible spectral region is 20 nm.

The positions of the bands of absorption of K_1 in the Chol- and SmA-phases of FELC (Fig. 2, curves 3 and 4, respectively) are close to those of the bands in the spectra of a benzene solution. In the SmC*-phase, the band of absorption of the dye is essentially broadened, bathochromically shifted, and split into two components (Fig. 2, curve 5). We may expect that, with increase in the viscosity of the matrix due to a decrease in its temperature, the probability of the formation of molecular aggregates of dye K_1 , e.g. dimers, increases.

The solutions of the dyes in FELC are homogeneous systems, i.e., molecules of a dye are distributed uniformly over the bulk of the matrix. The mass content of K_1 of 1.14% of the total mass of the solution is equivalent to the molar concentration of the dye of $4.5 \cdot 10^{-2}$ M. This is a rather great concentration, at which the dimers can be formed. In particular, in the Chol- and SmA-phases, the absorption of the dyes in the FELC matrix is conditioned by monomers and dimers.

According to [7], different configurations of dimers are possible: the coplanar configuration – monomers are positioned in parallel planes, the linear one – monomers are positioned in a single plane, and the obliquely coplanar configuration – molecules of the dyes are positioned in planes, the angle between which takes an intermediate value between 0° and 180° . In the spectra of absorption of coplanar and linear dimers, we observe a single band at the same directions of the vectors of dipole transition moments of monomers: the high-energy state for coplanar dimers and a low-energy state for linear ones. Spectrum 5 in Figure 2 testifies to two optically active states; hence, their configuration is obliquely coplanar.

On the cooling of FELC in the limits of the phase SmC*-phase (Fig. 2, curves 6 and 7), the splitting of the band of absorption of dye K_1 is conserved, but the intensity of absorption decreases, which is possibly caused by an increase in the scattering of light by the matrix or a change in the configuration of dimers of K_1 . The presence of the isosbestic point and the increase in the long-wave absorption with decrease in the temperature of specimens can be caused by the absorption in new, more complicated aggregates of K_1 .

The maximum of the band of photoluminescence of a solution of K_1 in toluene ($C = 2 \cdot 10^{-5}$ M) has a top in the region of wavelengths $\lambda_{\max} = 466$ nm. In the isotropic phase of FELC, this band shifts bathochromically by 13 nm (Fig. 3, curve 1). The analysis of its form in the Gauss approximation showed that it is composed from two bands: the intense band at $\lambda_{\max} = 479$ nm and the less intense one at $\lambda_{\max} = 516$ nm. The bathochromic shift of the integral band of photoluminescence of a solution of K_1 in FELC relative to the position of the band of the solution of K_1 in benzene indicates the increase in the interaction of excited molecules of the dye with molecules of LC.

On the subsequent transition from Chol- in SmA- and SmC*-phases, the intensity of the long-wave band of photoluminescence grows, and the intensity of the short-wave component somewhat decreases; as a result, the maximum of the integral band bathochromically shifts (Fig. 3, curves 2, 3, and 4, respectively).

In the solid phase of FELC, the band of photoluminescence of the dye has maxima at the wavelengths $\lambda_{\max} = 484$ and $\lambda_{\max} = 515$ nm.

In this case, the long-wave component has greater intensity (Fig. 3, curve 5).

The spectrum of photoluminescence of polycrystalline films of the dye produced by the application of the dye solution in dimethylformamide on the plates which are rapidly rotating (Fig. 3, curve 6) is broadened and significantly shifted to the long-wave side. The spectrum has three bands with the tops, λ_{\max} , at 515, 540, and 600 nm. The nature of these bands requires the additional studies.

The above-presented spectra of photoluminescence of solutions of the dyes and their analysis testify that the emission can be caused by the transitions from two excited states of dimers of K_1 . In the isotropic phase of FELC, their configuration is close to a coplanar one, and the high-energy component dominates in the spectrum. With decrease in the temperature of FELC (with increase in its viscosity), the configuration of dimers becomes obliquely coplanar. Such a configuration is manifested most clearly in the solid state of FELC. The angle between the straight lines which pass through the vectors of dipole transition moments can be determined by the formula

$$\varphi = 2 \operatorname{arctg} \frac{M_-}{M_+}, \quad (3)$$

where M_- and M_+ are the dipole transition moments of the short-wave and long-wave components of the spectra of absorption and luminescence. In the SmC^* -phase of FELC and in the solid matrix of FELC, it takes the values of 99° and 84° , respectively. Its mean value is about 90° ; hence, the vectors of dipole transition moments in monomeric dyes are almost mutually perpendicular.

The spectra of the polarization of emission are used in the determination of a relative arrangement of the oscillators of absorption and luminescence in the solutions of K_1 in FELC. According to the model of completely anisotropic oscillators [8,9], the degree of polarization P and the angle α between dipoles responsible for the absorption and luminescence are related to each other by the formula

$$P = \frac{3 \cos^2 \alpha - 1}{3 + \cos^2 \alpha} \quad (4)$$

which yields

$$\alpha = \frac{1}{2} \arccos \frac{7P - 1}{3 - P}. \quad (5)$$

The model of completely anisotropic oscillators has two versions: the static version (in which the absorption and emission is realized by different oscillators roughly oriented relative to the axis of a molecule) and the kinetic one (in which the absorption and emission is realized by the same oscillator which has time to turn by an angle α relative to the molecular axis during the absorption of a molecule in the excited state). For both versions, the methods of calculation of α are identical and are determined by the above-presented relation.

The studies of the polarization of the luminescence and dichroism of oriented films doped with dyes molecules of the dyes showed that the static model is most suitable to be used in the given case.

The analysis of the spectra of absorption, photoluminescence, degree of polarization P , and their changes under a variation of the phase of the liquid crystal matrix allows us to conclude that the splitting of the bands of absorption and photoluminescence of DMAEK dyes in the SmC^* - and solid phases of FELC is related to the fact that molecules of the dyes form obliquely collinear dimers in these media. As for the isotropic, Chol- and SmA-phases of the FELC-matrix, the bands of absorption and emission in the visible region of the spectrum are conditioned by monomers and linear dimers or dimers close to coplanar ones of the dyes.

In the figures, we give the experimental results of studies of dye K_1 . For dye K_2 , we observed the same regularities, and the difference in the structure of molecules leads only to a short-wave shift of the bands of absorption of K_2 by 10 nm.

For individual specimens, in addition to both a significant decrease in the intensity and a change in the form of the band of the light absorption by the dyes, we observe a deformation of the band of absorption by narrow bands, which have the interference character and can be caused by the interference processes in the SmA- and SmC^* -phases of the liquid crystal matrix (Fig. 6). By analogy with works [10, 11], a deformation of the spectra of a dye can be explained by the interference in the structures of dielectric materials with periodic modulation of the refractive index.

After the long-term irradiation of specimens by UV-light of a mercury lamp DRSh-250, we observed changes in the intensity and the form of the spectra of photoluminescence in DMAEK dyes which were partially described by us in [2]. At first, the light induces only the destruction of molecules of a dye which is accompanied by a redistribution of the intensities of the short-wave and long-wave bands. In this case, the spectra have the isosbestic point, whose presence testifies to the transition between two forms of radiating centers. After a longer irradiation of the solutions, we observed a decrease in the

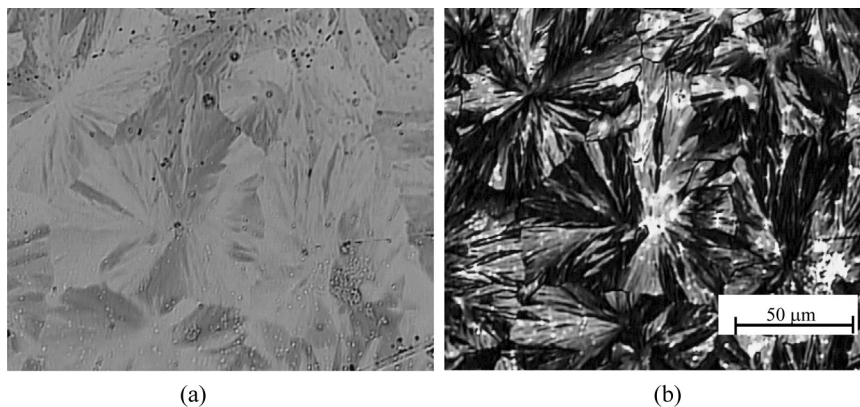


FIGURE 5 Photos of solid films of dye K_1 obtained by the application of a solution of the dye in dimethylformamide on the plates which are rapidly rotating in ordinary (a) and polarized (b) light.

intensity of luminescence in the whole spectrum. One of the stages of the process in isotropic solvents of DMAEK is the photoinduced crystallization of the dye.

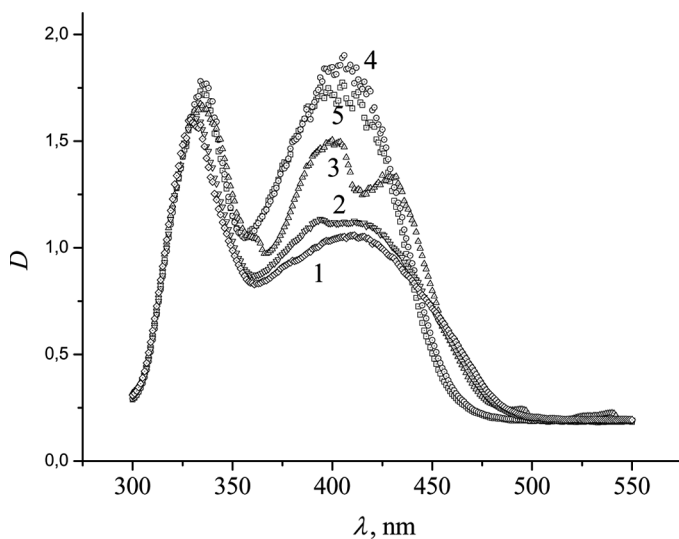


FIGURE 6 Spectra of absorption of thin layers of FELC with the admixture of dye K_1 at the temperatures $T = 317.6, 329.4, 334, 344.8,$ and 352 K, curves 1, 2, 3, 4, and 5, respectively.

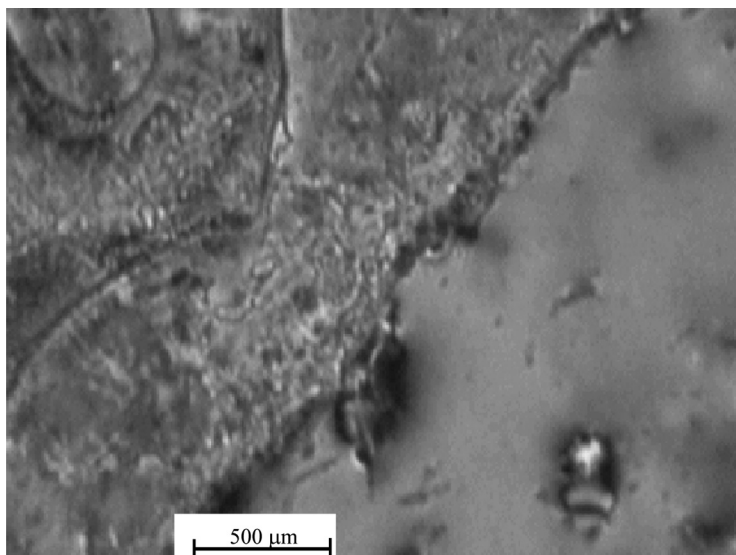


FIGURE 7 Photo of a dye solution in the liquid crystal matrix between glass plates with an orienter. The left part of a specimen is irradiated by UV-light, and the right part is non-irradiated.

The process of photoinduced changes is observed also on the irradiation of DMAEK dyes in the liquid crystal matrix. In this case, the formed crystallites due to a limitedness of the diffusion of molecules to the crystallization front are significantly less in size than those in the alcoholic solution, but they induce a sharp change in the orientation of molecules of LC.

In order to directly confirm the photodestruction of the dyes, the thin layers of FELC with an admixture of the dyes were covered by half with black paper and irradiated for 10 min. The photo (Fig. 7) demonstrates irradiated and non-irradiated parts of the same specimen, as well as a change in the orientation of the director in irradiated specimens.

In addition, it was revealed [1,3] that the irradiation induces a growth of dark electroconduction of specimens, which is an evidence of both the photochemical transformation of molecules and the creation of radicals which become charge carriers in solutions.

CONCLUSIONS

We have studied the spectra of absorption and photoluminescence of DMAEK-dyes in the FELC matrix at a dye concentration of 1.1–1.2 mass%. It is revealed that the change in the phase of the FELC matrix

induces sharp changes in the intensity, position, and form of the spectra of absorption and photoluminescence of DMAEK-dyes, whose molecules possess a prolate form. A slight increase in the light absorption intensity under cooling of specimens in the limits where the isotropic phase is preserved, its decrease by almost two times in the ordered phases, and changes of the form of the bands of absorption and photoluminescence which are especially significant in the smectic phase testify to the influence of a structure of the matrix on the intermolecular interaction of molecules of a dye, in particular, on the process of formation of dimers. In the oriented specimens, the spectra of photoluminescence of the dyes are partially polarized. In separate specimens, we have observed a deformation of the spectrum of absorption by narrow bands which have the interference character and can be induced by interference processes.

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