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Laser photolysis of fluorone dyes in a chitosan matrix

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Abstract. **Kinetics of laser-induced photobleaching of fluorone dyes (fluorescein, dibromofluorescein, eosin Y, erythrosin B, Rose Bengal) is studied in a chitosan matrix. For all dyes the bleaching kinetics at the intensities of laser radiation 0.7–11.9 W cm^{-2} demonstrates quasi-monomolecular behaviour. The results are analysed using a kinetic model, based on the four-level (S_0, S_1, T_1, T_n) scheme of the dye with chemically active triplet states taken into account. It is shown that the rate constants of the chemical reaction involving higher triplet states in the dyes studied amount to (3.9–18.6)×10^6 s^{-1} and exceed the analogous values for the reaction involving the first lower triplet states by nine orders of magnitude. The rate of reaction involving the first triplet states appeared to be higher by one–two orders of magnitude than that in the case of higher triplet states involved because of low population of the latter. The possible mechanism of dye bleaching with participation of chitosan that consists in reduction of the dye to the leuco form by transfer of hydrogen from the chitosan matrix is discussed.**

Keywords: *laser photolysis, fluorescein, dibromofluorescein, eosin Y, erythrosin B, Rose Bengal, chitosan, photobleaching kinetics, two-step absorption.*

1. Introduction

Photochemistry of fluorones that enter the wider class of xanthene dyes is actively discussed in literature [1–7]. The interest in photobleaching of dyes is caused by the possibility of its use in the physics of dye laser [8], in confocal microscopy (here the dye is a target bound to proteins or cell components) [9], in immunological analysis, in the technology of manufacturing light-sensitive media for optical recording of information (the photochemical event is the key stage of the formation of record elements) [10], and for accumulation of solar energy [11]. Photobleaching of fluorone dyes is commonly associated with redox reactions involving their triplet states [3].

The studied series of dyes (fluorescein, dibromofluorescein, eosin Y, erythrosin B, Rose Bengal) is interesting because in these dyes the probability of intersystem crossing to the first triplet state is variable within wide limits. This is caused by successive replacement of hydrogen atoms with heavier halogen atoms. In the present paper we study the kinetics of laser-induced (λ = 532 nm) photobleaching of fluorone dyes in the matrix of chitosan, well-known by its medical applications [12, 13]. Application of kinetic model of photoprocesses and the analysis of spectral fluorescent characteristics of the dye and the photoproduct allowed extraction of qualitative and quantitative information about the mechanisms of the photochemical reaction of fluorone dyes in the chitosan matrix.

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2. Materials and methods

2.1. Chemical agents

In the study we used sodium salts of the following fluorone dyes (Sigma Chemicals): fluorescein (Fl), eosin Y (Br_4-Fl), erythrosin B (I_4-Fl), Rose Bengal (I_4Cl_4-Fl). The dye 4′,5′-dibromo fluorescein (Br_2-Fl) (Fluka) was used in the acid form (Fig. 1a).

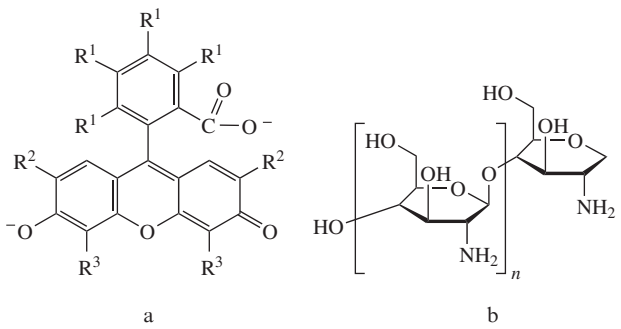

Figure 1. Structural formulas of dianions of fluorone dyes: fluorescein ($R^1 = R^2 = R^3 = H$), dibromofluorescein ($R^1 = R^2 = H$, $R^3 = Br$), eosin Y ($R^1 = H$, $R^2 = R^3 = Br$), erythrosin B ($R^1 = H$, $R^2 = R^3 = I$) and Rose Bengal ($R^1 = Cl$, $R^2 = R^3 = I$) (a), as well as chitosan (b).

To prepare films we used chitosan amino polysaccharide (2-amino-2-deoxy-β-D-glucan) with low viscosity (Fluka, Biochemica), dissolved in the 1% aqueous solution of acetic acid (Fig. 1b). The resulting solution was mixed with aqueous (for Br_2-Fl alcoholic) solution of dye and was deposited on a horizontal glass substrate. After drying at room temperature during two–three days the samples presented films ~10 μm thick with the concentration 0.25 wt.% (~10^{-3} M) of dyes in chitosan.

2.2. Experimental setup for laser photolysis

The dependence of optical density of the samples upon the laser exposure time was measured using the setup shown schemati-

cally in Fig. 2. The radiation from the Millenia 5s laser (*1*) was directed by the total internal refection prism (*2*) onto the light filter (*3*) that absorbed the radiation of the first harmonic (λ = 1.06 μm) and transmitted the radiation of the second harmonic (λ = 532 nm). The laser beam reflected by the glass plate (*4*) was incident on the FD-24K 5 photodiode, aimed to control the power of laser radiation during the procedure of sample transmission recording. The lens (*6*) with the focal length 8 cm produced a diverging beam in the region, where the sample was placed. The quarter-wave plate (*7*) transformed the linearly polarised radiation into the circularly polarised one. The axial part of the radiation beam was selected using the aperture (*8*) with the diameter 1.4 mm. At the distance 1 mm behind the aperture the sample (*9*) was placed with a system of its positioning in the plane, perpendicular to the laser beam axis. The radiation passed through the sample was detected with the FD-24K photodiode (*10*). Both photodetectors [(*5*) and (*10*)] operated in the diode regime with the supply voltage of 5V. The power of radiation incident on the sample was measured using the thermal 407A photodetector (Spectra-Physics) (*11*), which was installed at the sample location place. The electric signals from the detectors were measured and recorded using the programmable digital NI PXI 5122 12 oscilloscope. When planning the experiment, the theoretical estimates, formulated in Ref. [14], were taken into account.

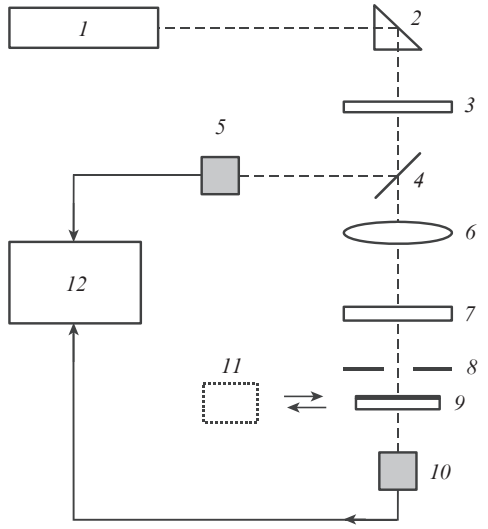

Figure 2. Schematic diagram of the experimental setup for laser photolysis (see comments in the text).

2.3. Instrumentation for spectral measurements

The absorption spectra were recorded using the Lambda 35 spectrophotometer (PerkinElmer, USA), while the spectra of fluorescence were recorded by means of the Fluorolog 3-22 spectrofluorimeter (Horiba Jobin Yvon, France). The fluorescence was excited at the wavelengths 460 nm (for Fl), 480 nm (for Br_2-Fl, Br_4-Fl), 490 nm (for I_4-Fl), and 505 nm (for I_4Cl_4-Fl) using the frontal excitation geometry. The obtained spectra were corrected taking the reabsorption and the spectral sensitivity of the recording system into account. All measurements were performed at room temperature.

3. Results and discussion

3.1. Experimental study of the photochemical reaction kinetics

The first absorption bands of the studied dyes lie in the visible spectral region, but are shifted with respect to each other (Fig. 3). The absorption cross section of the dyes (σ_1) at the wavelength 532 nm is maximal for Br_4-Fl, I_4-FL and by almost an order of magnitude smaller for I_4Cl_4-Fl and Fl. In all dyes under the action of cw laser radiation the effect of irreversible bleaching was observed.

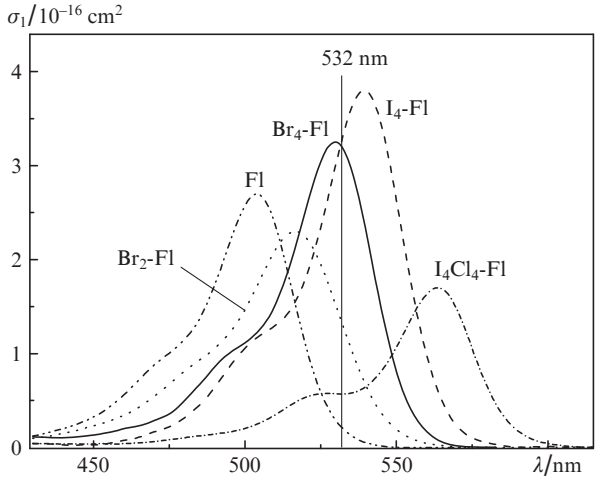

Figure 3. Absorption spectra of fluorone dyes in chitosan.

By the example of the samples with I_4-Fl, the kinetics of variation of the film optical density D under the action of laser radiation having different intensities is shown in Fig. 4, where from the optical density of the samples its background value at $t \to \infty$ is subtracted. It is significant that with the increase in the intensity the bleaching rate increases. The obtained time

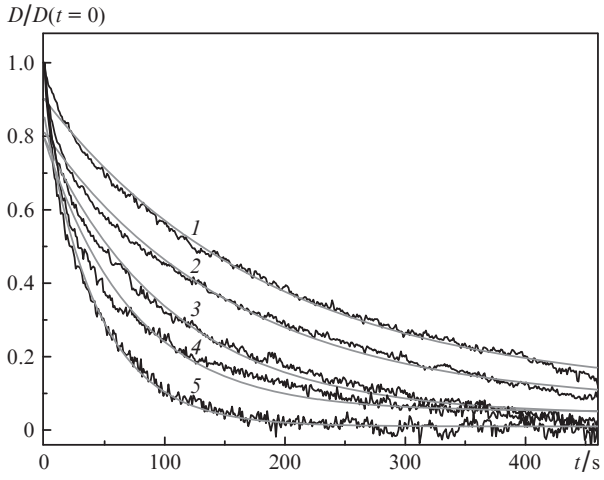

Figure 4. Dependences of the normalised optical density of I_4-Fl in chitosan films on the exposure time, the intensity of laser radiation being 0.7 (*1*); 1.9 (*2*); 4.5 (*3*); 7.9 (*4*), and 11.9 W cm^{-2} (*5*). Solid grey curves show the approximation by means of Eqn (1).

dependences of the optical density are satisfactorily described by the expression

$$\frac{D}{D(t=0)} = \exp(-kt), \tag{1}$$

which is an evidence in favour of the quasi-monomolecular mechanism of the chemical reaction. Similar results were obtained for samples of all fluorone dyes. In further analysis we use the observed rate constant of bleaching k (in s^{-1}) that characterises the exponential decrease in the optical density.

The dependences of the bleaching rate constant of fluorone dye films on the laser radiation intensity are resented in Fig. 5. It is seen that they possess nonlinear behaviour. The obtained results are discussed below with attraction of the kinetics model of photophysical processes and with the photochemical reaction taken into account.

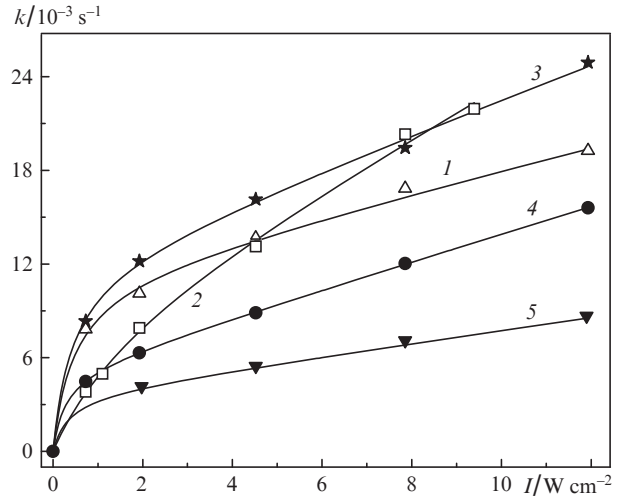

Figure 5. Dependences of the observed rate constant of bleaching k on the intensity of laser radiation, I, for dyes Fl (*1*), Br_2-Fl (*2*), Br_4-Fl (*3*), I_4-Fl (*4*), and I_4Cl_4-Fl (*5*).

3.2. Modelling the kinetics of photochemical reaction

To describe the laser-induced processes in a dye, we make use of the four-level scheme, shown in the extended Jablonski diagram (Fig. 6). The diagram includes the events of singlet–singlet (S_0–S_1) and triplet–triplet (T_1–T_n) absorption, fluorescence (S_1–S_0), quenching (S_1–S_0, T_1–S_0), intersystem crossing (S_1–T_1), phosphorescence (T_1–S_0), internal conversion (T_n–T_1), and photochemical reaction with the participation of triplet states T_1 and T_n. The scheme does not account for bimolecular processes of quenching of the excited states because of their low intensity, as well as for the chemical reaction involving the first singlet state because the lifetime of this state is essentially smaller than that of the first triplet state. The reverse intercombination transitions, not taken into account here, do not essentially affect the results of the calculations because of their low efficiency [15].

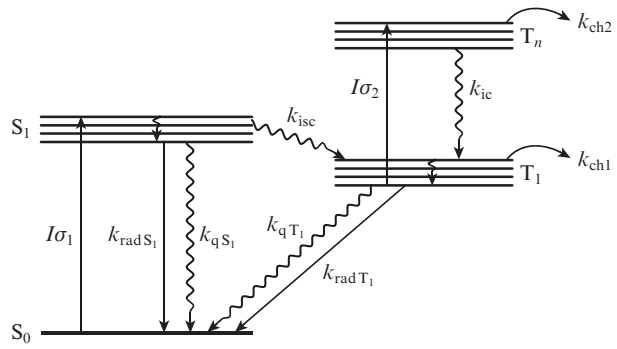

Figure 6. Jablonski diagram for a dye (see comments in the text).

The system of balance equations describing the laser-induced processes in the dye has the following form

$$\begin{aligned}
\frac{d[S_0]}{dt} &= -I\sigma_1[S_0] + (k_{radS_1} + k_{qS_1})[S_1] \\
&\quad + (k_{radT_1} + k_{qT_1})[T_1], \\
\frac{d[S_1]}{dt} &= I\sigma_1[S_0] - (k_{radS_1} + k_{isc} + k_{qS_1})[S_1], \\
\frac{d[T_1]}{dt} &= k_{isc}[S_1] - (k_{radT_1} + k_{qT_1} + I\sigma_2)[T_1] \\
&\quad + k_{ic}[T_n] - k_{ch1}[T_1], \\
\frac{d[T_n]}{dt} &= -(k_{ic} + k_{ch2})[T_n] + I\sigma_2[T_1].
\end{aligned} \tag{2}$$

Here $[S_0]$, $[S_1]$, $[T_1]$, $[T_n]$ are the populations of the ground, singlet and triplet excited states, normalised to the initial dye concentration; I is the intensity of laser radiation; σ_1 and σ_2 are the absorption cross sections for singlet–singlet and triplet–triplet transitions. In Eqns (2) we use the rate constants of the following processes: radiative ($k_{radS_1} = 1/\tau_{radS_1}$) and nonradiative transitions from the first singlet level, quenching (k_{qS_1}) and intersystem crossing T_1–S_1 (k_{isc}), radiative transition ($k_{radT_1} = 1/\tau_{radT_1}$) and nonradiative transition (quenching k_{qT_1}) from the first triplet state, internal conversion from highly excited states to the lowest triplet state (k_{ic}), photochemical reaction of the molecules with participation of the first (k_{ch1}) and higher (k_{ch2}) triplet states. All considered processes are monomolecular, and the corresponding rate constants are measured in s^{-1}.

The solution of Eqns (2) is found in the quasi-stationary approximation [16], corresponding to the cw laser irradiation and continuous recording of the transmission signal. In the calculation it is taken into account that during the time 10^{-1}–10^{-3} s a quasi-equilibrium distribution of populations is settled in the system due to fast photophysical processes. This distribution then slowly changes as a result of the photochemical reaction. The slow variation of the normalised optical density is described by the equation:

$$\frac{D}{D(t=0)} = \exp\left[-\alpha\left(k_{ch1} + \frac{k_{ch2}\sigma_2}{k_{ic}}I\right)t\right], \tag{3}$$

where

$$\alpha = \left[1 + \frac{(k_{radT_1} + k_{qT_1})(k_{radS_1} + k_{qS_1} + k_{isc})}{k_{isc}I\sigma_1}\right]^{-1}. \tag{4}$$

Introducing the notation $k_{radT_1} + k_{qT_1} = 1/\tau_{ph}$ и $k_{radS_1} + k_{qS_1} + k_{isc} = 1/\tau_{fl}$, we get

$$\alpha = \left(1 + \frac{1}{\tau_{ph}\tau_{fl}k_{isc}I\sigma_1}\right)^{-1}. \quad (5)$$

It is worth noting that the parameter α varies within the limits 0–1 and reaches 1 at the intensity of laser radiation corresponding to the saturation of the transition to the first triplet state. In a more complex situation, when $\alpha < 1$, the approximation of experimental dependences (Fig. 5) should be performed using Eqn (3), with Eqn (5) taken into account.

3.3. Discussion of the photochemical reaction kinetics

To analyse the experimental results (Fig. 5) we use the values of photophysical constants of fluorone dyes in a chitosan film, presented in Table 1. Using these values, the parameter α was calculated that appeared to be smaller than unity in the entire interval of intensities studied. The dependence of the observed photobleaching rate constant k on the intensity was approximated by means of Eqns (3) and (5), which allowed determination of the rate constants k_{ch1} and k_{ch2} of chemical reactions involving the first and highly-excited triplet states of the dye, respectively. From Table 1 it is seen that these constants differ essentially (nearly by nine orders of magnitude).

Let us use Eqn $[T_1]/[T_n] = k_q/(I\sigma_2)$ [16] to evaluate the ratio of populations of the first and higher triplet states in the process of photobleaching. In the studied intensity interval it amounts to 10^{10}–10^{11}. Taking the difference in rate constants of the photochemical reaction into account, we find that the rate of the reaction involving the first triplet states is higher by one–two orders of magnitude than that involving higher triplet states. Hence, in spite of the large rate constant for the molecules in higher triplet states, because of small population of these states the dominant contribution to the chemical reaction comes only from the first triplet states. In this case one should assume the existence of weakly bound hydrogen atoms in the sample with the threshold dissociation energy close to that of the first triplet state (see below). Increasing the pumping intensity by more than an order of magnitude as compared with the used in the present experiment will increase the yield of the chemical reaction involving the higher triplet state.

3.4. Discussion of the photobleaching mechanism

Among the possible mechanisms of laser-induced bleaching of dyes in polymer matrices in the absence of dopants, correcting the photochemical processes, the following ones are commonly discussed [2]: photobleaching of dye with participation of proton donor and electron donor groups, photobleaching as a result of bimolecular interaction of dye molecules in triplet state, dehalogenation.

In the present paper it is assumed that the bleaching of fluorone dyes is caused by their transition into the reduced form [3]. The transfer of protons to the dye molecule from the matrix (chitosan) occurs as a result of a sequence of the following events: the absorption of laser radiation by the singlet–singlet transition (S_0–S_1), intersystem crossing of the population into the first triplet state T_1 and the subsequent triplet-triplet absorption with population of the states T_n. In the process of photobleaching, the dyes come to the transparent form having no intense absorption spectrum in the visible region (Fig. 7). The coloured and the colourless forms are separated by the energy barrier, overcoming of which occurs at the expense of laser radiation energy. The formulated assumption is confirmed also by the analysis of spectral fluorescent properties of the initial dye and the photoproduct, the kinetics of the samples bleaching, and the energy balance of the photochemical reaction, which will be carried out below.

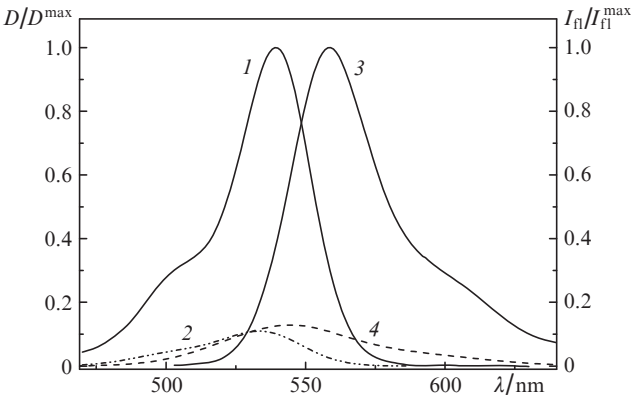

Figure 7. Absorption (*1*, *2*) and fluorescence (*3*, *4*) spectra of I_4-Fl in the chitosan matrix before (*1*, *3*) and after (*2*, *4*) 11-min irradiation.

3.4.1. Spectral fluorescent properties

The position of maxima in the absorption spectra before and after the exposure, as well as the reduction of the optical density of the photoproduct in the absorption band of the original form of the dye allow assumption that the initial dianion form of the dye turns into the neutral leuco form. In liquid solutions of fluorones the transition of the dye into the neutral colourless form is accompanied by the blue shift (by 5–20 nm for fluorescein, by 20–25 nm for eosin Y, and by 25 nm for erythrosin B) and by the essential decrease of the molar extinction coefficient (by 9–22 times for different dyes) [25, 26]. In solid solutions of fluorones in chitosan after irradiation during 11 min with the intensity 13 W cm^{-2} the analogous change in the absorption spectra takes place (for fluorescein the shift of bands is not observed, for dibromofluorescein it is equal to 9 nm, for eosin Y and erythrosin – to 6 nm, and for the Rose Bengal – to about 15 nm). The shift of the absorption band, related to the transition of the dye into the

Table 1. Photochemical and photophysical constants of fluorone dyes.

Dye	λ_{ph}^{max}/nm [17]	τ_{fl}/ns [18]	τ_{ph}/ms	k_{isc}/ 10^8 s^{-1}	σ_1(532 nm)/ 10^{-16} cm^2 [18]	α(0.7 W cm^{-2})–α(11.9 W cm^{-2})*	σ_2(532 nm)/ 10^{-17} cm^2	k_{ic}/ 10^{12} s^{-1}	k_{ch1}/ 10^{-3} s^{-1} **	$k_{ch2}k_{ic}^{-1}$/ 10^{-6} **	k_{ch2}/ 10^6 s^{-1} **
Fl	634	4.10	69 [19]	0.073***	0.21	0.07–0.58	2.6 [21]	1****	11.7±1.6	10.5±1.2	10.5
Br_2-Fl	684	2.62	4.44 [20]	0.67 [20]	1.33	0.15–0.77	3.5****	1****	11.6±2.0	16.9±2.9	16.9
Br_4-Fl	691	2.39	3.58 [20]	0.70 [20]	3.19	0.25–0.86	3.5 [22]	1 [23]	13.8±1.4	10.3±1.0	10.3
I_4-Fl	694	0.55	0.60 [20]	8.74 [20]	3.28	0.14–0.75	3.6 [22]	2 [23]	5.4±0.9	9.3±0.6	18.6
I_4Cl_4-Fl	741	0.85	0.28 [20]	8.04 [20]	0.57	0.02–0.26	3.9 [22]	1 [23]	3.9±1.1	3.9±0.7	3.9

* Calculated using Eqn (5); ** obtained by approximation of experimental data (Fig. 5) using Eqn (3); *** calculated using the formula $k_{isc} = \Phi_{isc}/\tau_{fl}$, where $\Phi_{isc} = 0.03$ [24]; **** taken to be equal the value for Br_4-Fl.

neutral lactone form is greater in aqueous solution than in polymer matrix, because the registered spectrum is the net absorption spectrum of the photoproduct and the initial form of the dye remaining after the exposure. As a result of the irradiation, the optical density of the samples was reduced by 4–11 times for different dyes. The residual optical density may indicate the presence of the initial dye.

The fluorescence spectrum of the exposed part of the film is changed in comparison with that of the intact film. Thus, as a result of the irradiation, the maximum of the spectrum is blue shifted: for fluorescein by 3 nm, for dibromofluorescein by 12 nm, for eosin Y by 10 nm, for erythrosin B by 14 nm, and for Rose Bengal by 5 nm. For the exposed and intact parts of the film the quantum yields of the fluorescence were estimated, which coincided for fluorescein and erythrosin B and appeared to be close for the rest of the dyes. These estimates may be due to the fact that the product of photobleaching does not fluoresce, as noted in [27, 28].

As shown using the quantum-chemical calculations of fluorone dianions, the high-intensity absorption band in the visible region of spectrum is caused by the tricyclic structure of the dye molecule. Sequential halogenation results in the red shift of electron absorption bands, keeping their intensity high and reducing the quantum yield of fluorescence [29], while dehalogenation leads to the blue shift of the spectral maximum and the increase in the fluorescence quantum yield [30]. These oppositely directed processes are not related to the photobleaching reaction that consists in photo-induced transition of the initial dye into the lactone leuco form.

3.4.2. Analysis of bleaching kinetics

Consider the mechanism of photobleaching as a result of bimolecular interaction of two dye molecules in the triplet state at a high concentration of the dye in the matrix. Two types of such interaction of exited molecules are possible, namely, the cooperative process and the triplet–triplet annihilation. In both cases short-range interaction is necessary (1.0–1.5 nm) and the result is the accumulation of excitation energies of two molecules. However, the estimation of the mean distance between molecules at the dye concentration $\sim 10^{-3}$ M yields ~14 nm. The localisation of dye molecules at the adjacent monomer groups of chitosan is possible, but requires experimental confirmation. It is possible to conclude that the discussed mechanism is hardly probable under the conditions considered.

In our case from the studies of reaction kinetics the quasi-monomolecular character of the reaction follows. This is typical for the case, when one of the reaction components is surplus. Such a surplus component may be the hydrogen of the biopolymer matrix.

3.4.3. Energy balance

Two-step excitation provides the energy enough to activate the bleaching reaction via a higher triplet state. To perform estimates let us use the data of Table 1. Indeed, the energy of the laser radiation quantum at the wavelength 532 nm is 226 kJ mol^{-1}, the absorption of the second quantum by the dye molecule, occupying the lowest vibrational level of the first triplet state allows attaining the excitation energy from 415 to 387 kJ mol^{-1} for the fluorone series from fluorescein to Rose Bengal, respectively. It is known that the energy of dissociating hydrogen from chitosan molecular groups amounts to 357–433 kJ mol^{-1}, which nearly corresponds to the excitation energy of higher triplet states of fluorones. The lowest rate constant of photobleaching was obtained for Rose Bengal, which also agrees with the experimental results [2]. This may be due to small energy of the triplet state insufficient for providing the dye molecules with the energy, required for more efficient course of photochemical reaction, in the process of two-step absorption.

A certain role in the process of the photochemical reaction may be played by hydrogen bonds in fluorone–polymer. It is known that a stronger hydrogen bond enhances the tendency towards the proton transfer [31]. Relatively small bleaching activation energies of fluorescein (7–21 kJ mol^{-1}) and Rose Bengal in polyvinyl alcohol (85 kJ mol^{-1}) [2], as well as eosin Y in gelatine (22 kJ mol^{-1}) [32] are comparable with the energies of neutral and ion hydrogen bonds. Therefore, the formation of intermolecular hydrogen bonds in fluorone–chitosan may reduce the hydrogen dissociation energy in the photobleaching reaction.

3.4.4. The role of chitosan in the process of fluorone bleaching

Since the amino compounds are quenchers of the excited states of different multiplicity [2], the chitosan amino groups are expected to reduce the photobleaching rate of fluorones. The authors of [32] studied photobleaching of eosin Y in three polymer matrices with different content of amino groups (polyvinyl butyral, gelatine, and chitosan). It was shown that the effective rate constant of the dye bleaching by the radiation of the argon laser (λ = 488 nm) decreases by an order of magnitude when passing from polyvinyl butyral to chitosan. Hence, the hydrogen bond formation and the quenching by amino groups are competing processes in the course of photobleaching of a dye in chitosan.

4. Conclusions

Thus, we have performed a comprehensive analysis of laser photobleaching of solid solutions of five fluorone dyes in a chitosan matrix using spectral and photophysical methods, as well as kinetics calculations. We have shown that under the conditions of the experiment the mechanism of photobleaching with participation of the first triplet states is implemented. Higher triple states, obtained by two-step laser excitation, will essentially contribute to the process at the intensities higher than 100 W cm^{-2}. The interaction of the dye with the chitosan matrix in the process of photobleaching may correct the energy balance of reaction at the expense of hydrogen bonds formation. It may also reduce the population of the excited states due to their quenching by amino groups. Relatively small rate constant of photobleaching with participation of higher triplet states in Rose Bengal is associated with lower energy of the first triplet level, which does not provide enough energy for efficient reaction under the conditions of two-step excitation.

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