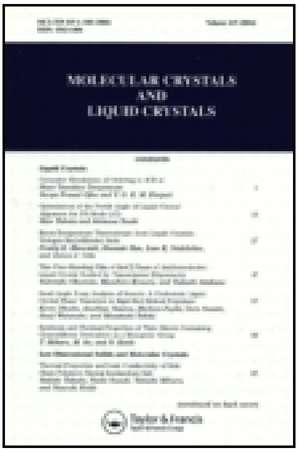

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Spectroscopic Manifestation of Dye Pair Interactions at High Concentrations in Structurally Organized SiO_2 Films

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The concentration dependence of the spectra of ionic and neutral dyes encapsulated in mesoporous silicate films is studied. A mesoporous dyed SiO_2 *film was prepared by the sol-gel technology with the use of amphiphilic three-block copolymer Pluronic P123 as a surfactant. It is found that if the dye concentration exceeds the mesoporous one, the new spectral bands appear that are distinct from those of initial monomolecular predecessors. To explain the phenomenon, it is assumed and proved that the origin of new spectra is due to the formation of ionic pairs, excimers, and excitons with participation of dye molecules localized at the characteristic places of the mesoporous silicate film.*

Keywords Dye fluorescence; excimers; ionic pair; mesoporous silicate film; polymer micelles

Introduction

For a long time, the organic dyes have occupied the extensive spheres of applications. Nevertheless, they remained as objects of the incessant scientific attention up to nowadays. In particular, the applications of dyes in the laser physics and optics [1] have boosted the development of the sol-gel technology aimed at the production of organically modified silicates (ormosil) having *a priori* the best thermooptical parameters as compared with those of polymeric matrices [2]. In work [3], it was found that the photochemical stability of covalently bound dyes in ormosil is higher than that in the case of van der Waals bonds in solutions.

Another technology of the encapsulation of an organic dye in a glass matrix has originated in connection with the production of porous and mesoporous silicate glasses which are characterized by accidentally or regularly organized pores. For manufacturing the similar porous matrices the methods of acid-alkaline etching of soda-borate-silicate glasses were developed [4]. The entry of a dye into a matrix occurs by means of its sorption from a solution. Because the ionic dyes get the necessary spectroscopic parameters only in polar solvents, pores of such a matrix should

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be filled with the corresponding solvent. The laser application of similar dyed mesoporous structures for the light oscillation was carried out in [5].

For the first time, the regular mesopores in silicate glasses prepared by the sol-gel technology were obtained in [6,7]. Then the application of nonionic di- and three-block copolymers, surfactants of a new generation, was started with a special purpose in [8]. The ability of amphiphilic molecules to a self-assembly in water solutions into modular structures – micelles – with a subsequent self-organization of micelles in spatially ranked ensembles of various symmetries plays the dominant role in the given approach. At the first stages of studies, only some simple ionic surfactants (ammonix LO) capable to raise the dye solubility and thereby to interfere their dimerization to conserve the fluorescence quantum yield were available. Today, their assortment is quite wide and is characterized by the extensive actual and perspective technical/medical applications. The well-defined block copolymer surfactants undergo the self-assembly in aqueous solutions in order to minimize the energetically unfavorable hydrophobic interactions. In accordance with the theoretical model [9], specific self-assembled nanostructures can be targeted according to a dimensionless «packing parameter» $\mathbf{p}$ which is defined by the following relation: $\mathbf{p} = \mathbf{v}/\mathbf{al}$, where $\mathbf{v}$ is the volume of hydrophobic chains, $\mathbf{a}$ is the optimal area of a head group, and $\mathbf{l}$ is the length of a hydrophobic tail. Therefore, the packing parameter $\mathbf{p}$ of a given amphiphilic molecule usually dictates its most likely self-assembled morphology.

Generally, spherical micelles are favored for $\mathbf{p} < 1/3$, cylindrical ones for $1/3 < \mathbf{p} < 1/2$ and enclosed membrane structures (vesicles, also known as polymersomes) for $1/2 < \mathbf{p} < 1$.

Statement and Motivation of Studies

Studying the spectroscopic behavior of ionic, neutral, and zwitterionic dyes (one representative from the termed group) at extremely high achievable concentrations in structurally ranked silicate films (SRSF) was the purpose of the given research. SRSF of nanometrical thickness were prepared by the sol-gel technology with use the surfactant Pluronic P123. The hydrophobic nature of the surfactant can be utilized for the strong solubilization of organic compounds, and the one-dimensionality enables us to design a well-aligned molecular system inside the hydrophobic nanochannels. In the literature, some spectral changes in fluorescence bands of Rhodamine 6G dye at a high concentration in structured mesoporous silicate films were reported without any explanation of the observable effect [10]. The most studied and understood feature for similar materials is an enhancement of the electronic energy transfer between donor-acceptor pairs in accordance with the Förster model at the localization of a molecular pair in a micelle or nearby [11,12]. In general, our statement of the problem is similar to that in [12] with such a distinction that authors [12] used the ionic polymeric compound cetyltrimethylammonium bromide (CTAB) as a surfactant, while we have used Pluronix P123.

Preparation and Testing of Samples

Mesoporous SiO_2-films were produced by the sol-gel synthesis in the presence of nonionic three-block copolymer $PEO_{20}PPO_{70}$ PEO_{20} (Pluronic P123, Sigma Aldrich, m.w. 5800) as a surfactant. In the used technology, two separately prepared solutions are mixed and deposited on substrates at their gyration (spin-coating) or drive (dip-coating) with a subsequent drying at room temperature and a constant dampness. The sol-solution was plotted on the base of chemically pure tetraetoxy silane ($Si(OC_2H_5)_4 \equiv$(TEOS), ethanol, twice distilled water, and a 35% HCl solution. After the hydrolysis and the sol production, the earlier prepared gel-solution of termed dyed surfactant Pluronic P123 at the first critical concentration was added to this solution, which caused the spatial self-assembling of already existing micelles. The ratio of the concentrations of gel-intermixtures (dye and Pluronic P123) in gram-molecule units varied from 1:32 to 32:1. The basic regular composition of the material was described by the following relation of molar concentrations: $TEOS{:}C_2H_5OH{:}HCl{:}H_2O = 1{:}20{:}0.5{:}8$. The necessary aging degree of the terminated intermixture was reached during $(40 \div 60)$ min at the continuous stirring. Then, by the above-mentioned actions, the film deposition at gyration/drive velocities of 2040 rpm/(0.1 – 20) cm/min was carried out on the purified glass substrates (or others materials). The obtained liquid film dried at the regular temperature/damp formed a firm silicate coating 100–250 nm in thickness on the used substrate. Owing to the evaporation of the liquid water fraction during the drying, the concentration of dyed micelles in the film increased to the second critical value. Due to that, their spatial streamlining took place. Simultaneously, the porous grid structure SiO_2 with a wall thickness of $(3 \div 5)$ nm was formed around spatially ordered dyed micelle. For the specified small thickness of films, the streamlining of micelles occurs simultaneously in the plane of a film and over its thickness with the formation of cylindrical columns directed normally to the developed film plane. At the intended conservation of the organic micelles in the obtained film, this silicate structure is termed the mesoporous one. The heating of samples to 500°C is accompanied by the evaporation of organic micelles and the formation of truly porous silicate films.

The formation of a ranked structure in films was tested by methods of the small angular X-ray diffraction. The results of tests obtained with a diffractometer DRON-3 M are presented in Figure 1. They confirm the formation of the ordered structure and its structure invariance at the use of nonamphiphilic dyes.

The IR spectroscopy indicates the almost full elimination of water from the ready films. The film thickness measured by methods of atomic force microscopy was found systematically in the interval (180–220) nm at the invariance of embodying the featured technology.

The following evident estimates allow us to determine the key parametres of self-assembly spatial structures. The wavelength of X-ray radiation from the tube with a copper cathode is $\lambda_{CuK\alpha} = 1.5405$ Å. The Bragg conditions $m\lambda = 2\Lambda\sin(\Theta_m)$ for the angular positions of diffraction peaks lead to the spatial periods of 2D structures $\Lambda_1 = 102.04$ Å and $\Lambda_2 = 101.55$ Å for $m = 1$ and 2, respectively. The additional registered maximum in Figure 1 is possibly related to the hexagonal symmetry of a micelle self-organization. It is also seen that the introduction of ionic dye R6G in the gel fraction did not destroy the arising ordered SiO_2 structure.

Due to the ordering and since the spatial period of the ordered SiO_2 film structure is spotted by spherical micelle sizes owing to a dense packing, the micelle concentration at the cubic symmetry is determined as $\approx 10^{18}\,\mathrm{cm}^{-3}$. For the denser hexagonal packing, one can consider the concentration of micelles to be approximately by one order higher. From the data in Figure 2 on the optical density $\mathbf{D} = \mathbf{c\varepsilon T} = 1.5$ for R6G with its molar extinction $\varepsilon_{max} = 118 \cdot 10^3$ and the film thickness $T = 200$ nm, it is possible to calculate the dye concentration equal to $0.6\,\mathrm{mol/l} = 3.6 \cdot 10^{20}\,\mathrm{cm}^{-3}$. The comparision of the concentrations of micelles and dye by the data

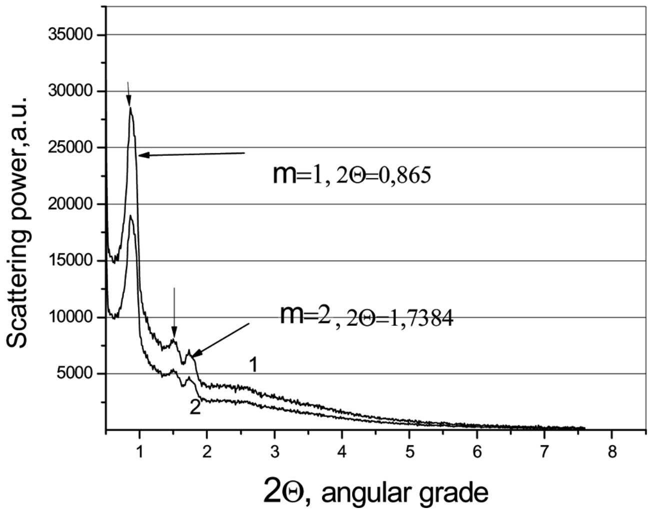


Figure 1. Diffractogram of SRSF without R6G (the upper dependence) and with R6G (the bottom dependence).

in Figure 2 allows us to conclude that the tenfold excess of the concentration of dye over that of micelles does not still lead to optically registered interactions between dye molecules in the basic state, which would be felt by the optical absorption spectroscopy.

The preliminary conclusion from the obtained relation between the concentrations of dye and micelles can be formulated as the following assumption: all dissolved dye in gel is not implanted in micelles of a silicate film. Its part exceeding the limiting dissolvent power of micelles P123 can be placed in the thermodynamically labile interface region between silicate walls and micelles. It is most likely that

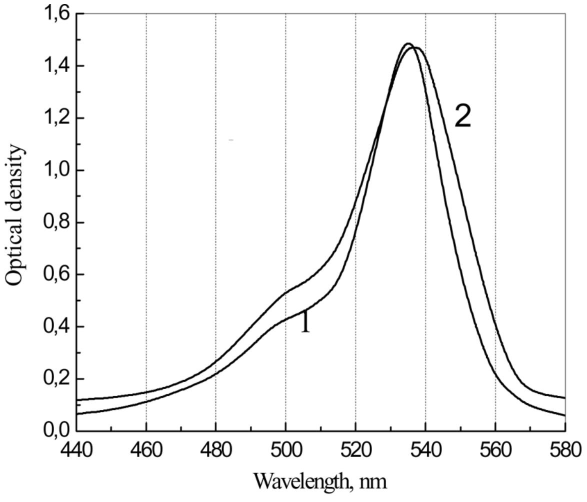


Figure 2. Absorption spectra of R6G in SRSF (1) and polyurethanacrylate (2) at identical optical densities, but at concentrations which differ by several orders of magnitude.

the initially homogeneous dye distribution in a film is broken due to the diffusion redistribution of dye with a positive gradient to the periphery. This is especially appreciable on samples at concentrations exceeding the limiting value of 0.5 mol/l.

Results and Discussion

The subsequent results trace changes in absorption/fluorescence spectra of the following dyes – ionic R6G, neutral 6-aminophenalemen and zwitterionic pyrromethane PM580 with increase in the concentration of P123 in SRSF and gel at room temperature. The used method of analysis promotes the qualitative understanding of the nature of the registered changes in interrelation with the probable localization of ions and uncharged molecules in SRSF. In Figure 3, we present the evolution of the absorption spectrum of R6G: curve 1 corresponds to the upper concentration limit, at which the monomolecular fraction exists preferentially; curves 2, 3, and 4 show changes at the excess of concentrations. Changes develop with a peak at a wavelength of 510 nm as compared with the standard peak of R6G in a polar solvent at 535 nm.

The observed behavior of the R6G spectrum does not suggest to consider the absorption peak at 510 nm as that related to vibronic oscillations of a π-electron conjugation chain, as it is habitually accepted. It is more likely to connect the peak with a specificity of charged states of ionic dyes, in particular, a cation-anion R6G pair under conditions of the incomplete ionization as opposite to the typical state R6G in polar solvents at the full ionization of two ions. By applying the mathematical procedure of deconvolution, we expand the obtained integrated contours into 2 Gaussian components, whose weight contributions change with the variation of the concentration of R6G, but the wavelength peak position is conserved. The long-wave absorption band can be referred to the known absorption spectrum of

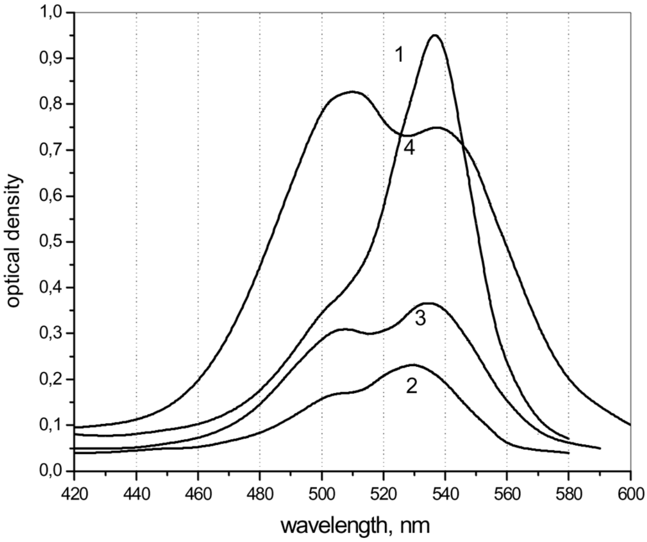
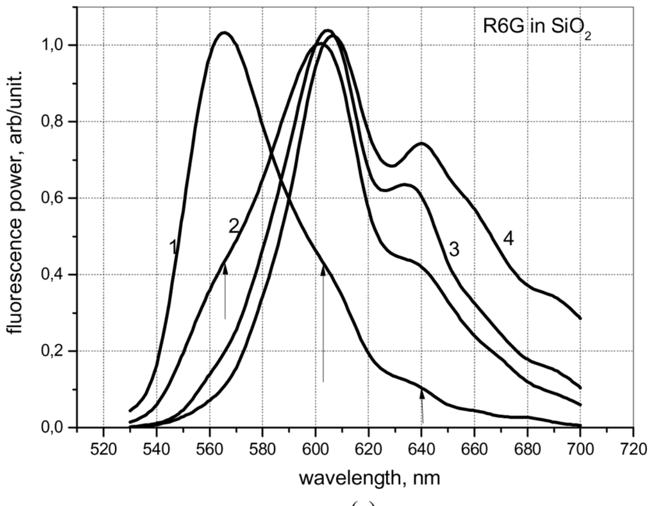


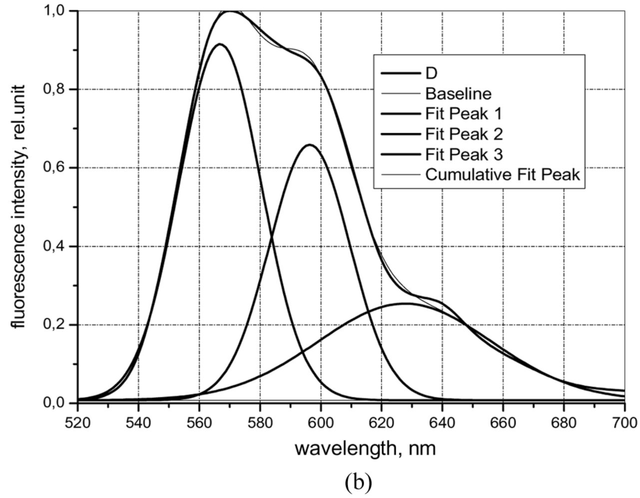
Figure 3. Evolution of the absorption spectrum of R6G with increase in the concentration in SRSF: 1 – ≈0.5 mol/l; 2, 3, 4 – >0.5 mol/l.

R6G cations, whereas a short-wave band should be reasonably assigned to ionic pairs. The weight contribution of this center depends on the dye concentration. The mathematical analysis supports the assumption about the two-center nature of the absorption spectrum of R6G at concentrations above 0.5 mol/l in SRSF with the used preparation technology.

The behavior of the fluorescence spectrum of R6G at a change of its concentration in SRSF testifies to the multicenter character as well. The fluorescence spectrum of R6G in SRSF presented in Figure 4a shows a number of unusual features. Contour 1 is related to the typical cationic spectrum of R6G in polar solvents. The contour asperities on its long-wave wing, being absent usually in a cation fluorescence band of the dye in polar solutions, appear here already at the critical



(a)



(b)

Figure 4. (a) Evolution of the fluorescence spectra of R6G in SRSF with increase in the concentration: 1 – concentration below 0.5 mol/l, 2, 3, 4 – concentrations above 0.5 mol/l, (b) deconvolution of the integrated fluorescence spectrum into three Gaussian components.

concentration (~0.5 mol/l). It is also impossible to consider them as a manifestation of vibronic interactions of π-electronic oscillators with vibrations of the molecular skeleton in the excited electronic state: the concentration dependence of the weight contribution of these contours testifies to their multicenter origin.

The deconvolution of the integrated fluorescence contour into Gaussian components is presented in Figure 4b. It is seen also that, at some excess of the critical dye concentration, the main contour of the cation R6G fluorescence disappears completely, and there is only a feeble hint at its former existence (the mark on the left wing of contour 2).

The fluorescence quantum yield of R6G in SRSF at these concentrations (always higher than those of usual solutions) decreases strongly, but the remained fluorescence power is enough to be registered by the standard technique even at the further growth of the concentration up to the case of a polycrystalline powder. Fluorescence spectra were registered by a spectrometer (Hitachi MPF-4)) under conditions of the excitation at 530 nm, which corresponds to the absorption peak of cation R6G, and in the light reflection configuration to diminish the reabsorption shifts.

So, the fluorescence band with a peak at 605 nm grows from the first inflexion on curve 1 (it is marked by the arrow). The band contour does not vary anymore, as the concentration grows, but the increase of the concentration causes a growth of the intensity of the second fluorescence band with a peak at 640 nm from the second marked inflexion on the initiating fluorescence band.

The R6G emission spectra registered with a more sensitive spectrometer at the highest concentrations are presented in Figure 5. Here, the fluorescence spectrum of polycrystalline R6G (5) is presented also. Coinciding by the red shift direction with the spectra of R6G for the highest concentrations in SRSF, this crystalline R6G spectrum has a considerably narrower spectral width. The last specifies the

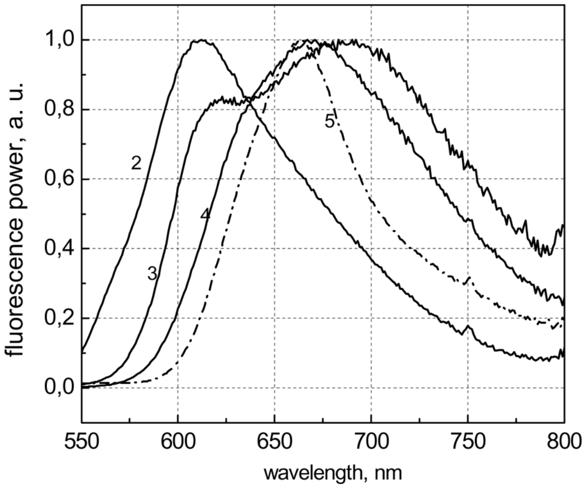


Figure 5. Fluorescence spectra of R6G in SRSF at various concentrations and in the polycrystalline phase: contour 2 with a maximum at 605 nm, contours 3 and 4 – limiting concentrations; a maximum at 670 nm which is characteristic of the fluorescence in the polycrystalline phase of R6G prevails (contour 5).

higher degree of streamlining and homogeneity of fluorescence centers (dye molecules) in the case of a natural crystal in comparison with the quasicrystal streamlining in SRSF.

The multicenter character of the fluorescence spectra is supported also by the measurement of lifetimes within integrated contour 3 (Fig. 5). In Figures 6a–d, we present the data measured with the use of picosecond pulses of a 357-nm laser for the fluorescence excitation. The fluorescence lifetime of R6G in the polycrystalline phase is equal to 2.7 ns. The lifetimes of monomolecular R6G cations and a fluorescence center characterized by a peak at 605 nm (contours 2 and 3 in Fig. 5) in SRSF are equal to 2.8 ns and 3.5 ns, respectively, which is explainable as the presence of spectrally imposed 2 bands from two centers of different origins. The lifetimes of the fluorescence centers related to spectrum 4 in Figure 5 at 640 and 670 nm are equal to 2.2 and 2.5 ns.

The obtained data allow us to draw conclusion about the multicenter origin of fluorescence registered at the highest concentrations of R6G in SRSF above 0.5 mol/l.

The similar features of changes in the absorption/fluorescence spectra were observed for zwitterionic dye PM580 (Fig. 7), whose intermolecular ionization and, respectively, the position of absorption bands depend on the environment polarity or, other words, on the localization of molecules in SRSF.

Meanwhile in the gel solution of P123, the forms of absorption bands of R6G and PM580 were not changed in a wide interval of concentrations and coincided with contours 1, 5 in Figures 2 and 7 for low concentrations. The neutral aminophenalemine discovered no changes in the form of initial absorption bands in wide limits of the dye concentration in SRSF.

A spectral inhomogeneous broadening in the case under consideration is not simply related to the casual character of a local field similar to the case of rare-earth ions in the common glass matrix. In the typical case of a nonuniform spectral broadening, a continuous shift of the transition frequency for the base center takes place. In the case under consideration, there is the formation of 2–3 centers with the own resonant transition frequencies. The main reason for the occurrence of several centers consists in different possibilities for the dye localization in a structurally ranked silicate due to the significant polymeric micelle ordering in a film and the subsequent pair interactions of dye ions (molecules) in the ground and excited states. Therefore, we now discuss the possible places of localization of the studied dyes in SRSF.

For a long time, it was established reliably that surfactant molecules increase the dye solubility and interfere the aggregation of dye molecules in water solutions. The reason for a similar activity consists in the formation of direct (or inverse) micelles, whose exterior spherical (or cylindrical) parts possess the hydrophilic ability, whereas the interior part of a micelle shows hydrophobic properties. For ionic dyes (R6G and the majority of dyes), the inorganic anion is hydrophilic, while the cation responsible for optical parameters is partially hydrophobic. Both ions are coupled by the Coulomb interaction force. The minimization of the electrostatic energy for a dye and the solution will be reached, if the cation is localized in a hydrophobic core of a micelle, and the anion is positioned in a hydrophilic shell. In [13], this ability was used for the extraction of an organic ionic dye from a solution in SRSF on the base of ionic surfactant CTAB. It was established that, for the effective extraction, the ion charge sign has prevailing meaning. Unlike CTAB

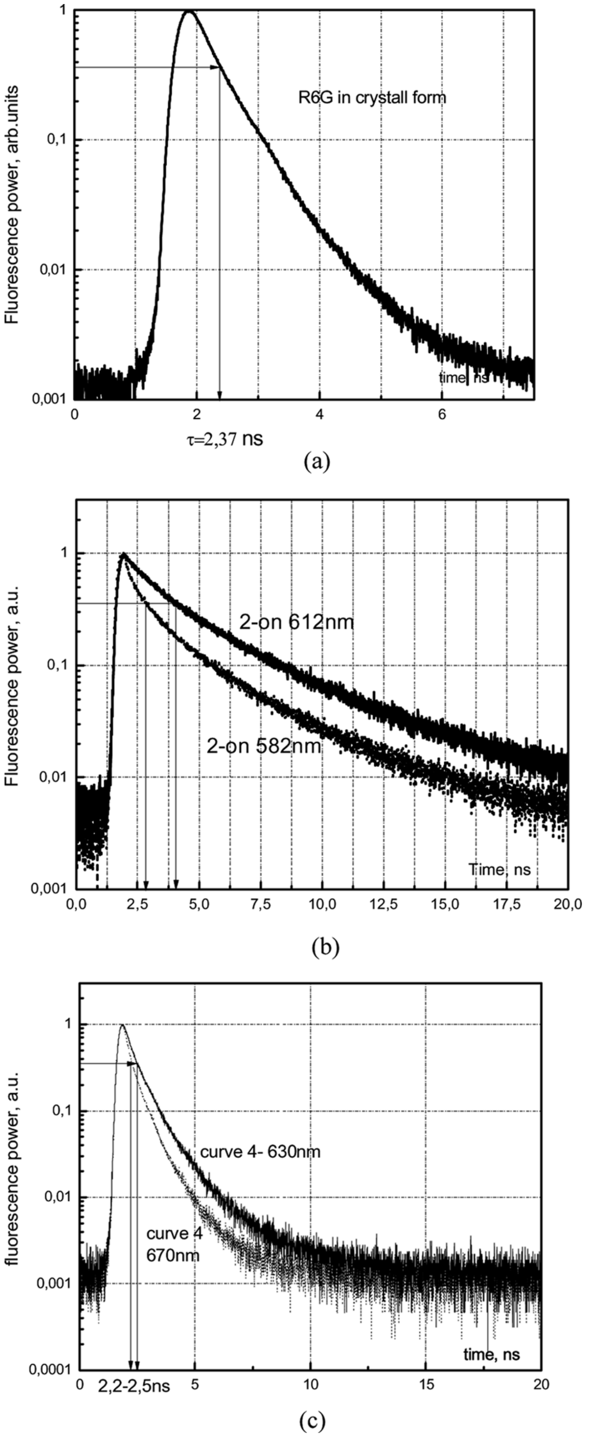


Figure 6. Fluorescence lifetimes at various wavelengths for the integrated spectra in Figure 5: (a) contour 5, 670 nm; (b) contour 2, 582 and 612 nm; (c) contour 4, 630 and 670 nm.

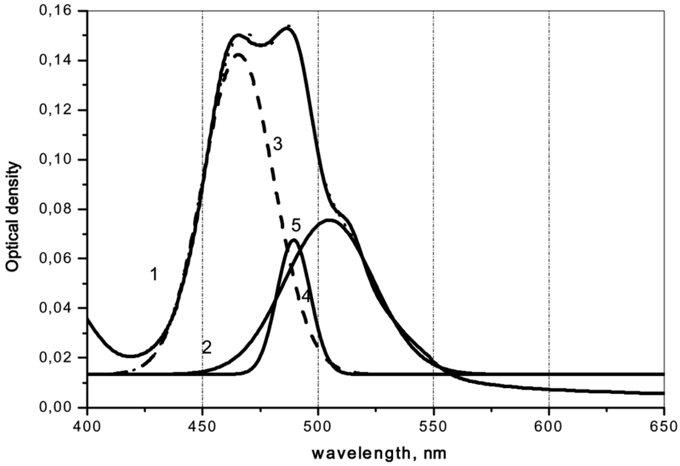


Figure 7. Absorption spectrum of PM580 in SRSF (1) and its deconvolution into three Gaussian components (3, 4, 5) as a possible proof of the presence of several centers, 2 – restitution of initial integrated contour with correlation factor COD (R^2) = 0.954.

micelles with a rather small core, the core and the shell of pluronic P123 micelles are large and loose-packed. Therefore, such a micelle core can "hide" some dye organic cations. This property of micelles is termed as solubility, but the number of molecules accepted inside is evidently limited. Therefore, as the above-mentioned concentration of 0.5 mol/l is achieved, the hydrophobic core is saturated by cations. Further, they are forced to search a place on the shell periphery, which is energy-unfavorable. That is why the diffusion redistribution of the dye concentration from homogeneous to inhomogeneous with a gradient in the direction to the periphery of a silicate film takes place. Probably, the ionic pairs with their characteristic absorption spectrum appear and are localized on the silicate wall – micelle shell interface.

For anion dyes, the concentration dependence of spectra under similar conditions will be definitely different, and this point is under study now. Zwitterionic dye PM580 forms a three-component spectrum in SRSF which is more complicated than that of R6G, and its detailed study still will be of interest (Fig. 7).

The nonionic dyes are characterized by the weak van der Waals interaction that cannot be observed in the ground state, while the interaction in the vibronic excited state can reveal itself as the excimer/exciplex fluorescence.

A possibility of the contribution of excimer fluorescence to the complicated spectra of R6G at higher concentrations has been specified partially, because the basic fluorescence band is weak and disappears with increase in the concentration (Figs. 4 and 5). Simultaneously, the new band 2 with a peak at 605–610 nm appears, and its intensity grows without changes of the contour. For the excimer formation, it will be enough to localize at least 2 dye cations in a micelle core, like the known pirene excimer fluorescence originated at high concentrations even in an ordinary solution [14].

The appearance of the fluorescence emission with a peak at 670 nm and its approximate coincidence with the fluorescence band of a crystal R6G allow us to refer it to the excitonic states of R6G in SRSF.

Conclusions

We have studied the evolution of absorption/fluorescence spectra of dyes of three types (with different nature of a charge state) at varying concentrations in structurally ranked silicate films with mesopores on the basis of three-block copolymer Pluronic P123. It is found that the monomolecular nature spectrum absorption/fluorescence is supported only up to a certain concentration (≈ 0.5 mol/l). The excess of this limit is accompanied by the accruing changes.

The suggestion about a physical nature of the observed spectral changes is formulated. It is related to the amount of organic cations which can be localized in the hydrophobic micelle core with their counterions in the hydrophilic micelle shell. At the excess of the admissible «micelle» concentration, the formation of ionic dye pairs on the silicate walls – micelle shell interface and the appearance of the absorption spectrum of ionic pairs take place. The share of the absorption band of ionic pairs in the absorption spectrum of R6G in SRSF near 500 nm accrues monotonously with increase in the dye concentration.

The dye localization on the interface is thermodynamically not suitable owing to the diffusion redistribution of the embeded dye, and its transport to the periphery of samples is observed.

If the number of R6G cations in a hydrophobic core is more than two, the formation of excimers and the excimer fluorescence with the characteristic spectrum and lifetime are observed at the simultaneous supression of the known monomolecular fluorescent spectrum. Accordingly, the synchronous suppression of the basic band of R6G at 565 nm, as well as the relative increase of the excimer fluorescence band intensity at 610 nm and the exciton emission at 670 nm, is observed. The possible exciton nature of the emission of R6G in SRSF at higher concentrations is indicated by the coincidence of the given spectrum with that of an R6G polycrystal.

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