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PHOTOCHEMISTRY AND MAGNETOCHEMISTRY

Preparation and Properties of Nanosized Fluorescent Solid Films Based on a Polyelectrolyte–Surfactant Complex with Organic Dyes

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Abstract—A procedure for preparing an organosoluble stoichiometric complex based on a cationic polyelectrolyte and an anionic surfactant is described. A method is proposed for forming monolayers at the water–air interface, along with conditions for preparing fluorescent nanosized solid films based on polyelectrolyte complex and organic dyes using the Langmuir–Blodgett (LB) method. The spectral and luminescent properties of the obtained films are investigated. It is established from the absorption and fluorescence spectra of LB films that electrostatic interaction between the molecules of polyelectrolyte complex and oxazine dyes results in dimer formation.

Keywords: Langmuir–Blodgett films; polyelectrolyte; dye; optical properties.

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INTRODUCTION

Polyelectrolyte–surfactant complexes are a new type of materials that allow us to produce targeted effects on the processes of supramolecular structure formation and control the macroscopic properties of materials on the molecular level. The preparation, conformational and physicochemical properties of these complexes were reviewed in [1, 2]. The Langmuir–Blodgett (LB) technique is one method for forming functional nanomaterials. This method has certain specific features. In particular, amphiphilic molecules or a mixture of nonamphiphilic compounds with surface-active fatty acids and polymers are typical objects of the LB technique [3–5].

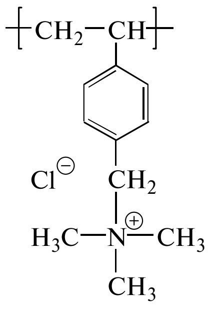
Assembly due to noncovalent bonds (e.g., electrostatic interaction) has undoubted advantages over chemical synthesis, which involves labor intensive and cost-consuming preparation procedures. The obtained systems can be subjected to reversible structure changes in response to environmental changes (e.g., solvent, component concentration, temperature, and so on) [6–8]. Structured materials obtained using different methods of self-organization and molecular recognition form the basis for constructing responsive nanomaterials [9, 10]. Despite the reports in the literature from different authors on investigating the physicochemical properties of such materials in the form of adsorbed films or Langmuir monolayers [11, 12], there are virtually no studies on preparing fluorescent thin solid films from polyelectrolyte–surfactant complexes and dyes.

A method for forming monolayers at a water–air interface is proposed in this work, along with the conditions for preparing fluorescent nanosized films based on polyelectrolyte complexes and dyes of the oxazine group via the Langmuir–Blodgett method. It is assumed that the electrostatic interaction between a polyelectrolyte complex and dye molecules will facilitate the formation of LB films. Depending on the distribution of the electron density of the dye molecules, changes in the electrostatic interaction of a polyelectrolyte complex and a dye are expected that will affect the coefficient of a dye molecule's transition to the substrate. The dyes of oxazine group is widely used as an active material in photodiodes and lasers [13, 14], in solar energy concentrators [15], and in sensors of the medium polarity [16, 17].

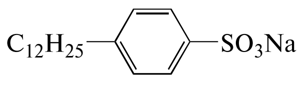
EXPERIMENTAL

A stoichiometric polyelectrolyte–surfactant complex was prepared from a cationic polyelectrolyte, poly-N-vinylbenzyl-N,N,N-trimethylammonium chloride (PVBTMAC) with molecular weight $M = 2.47 \times 10^4$, and an anionic surfactant, sodium dodecylbenzenesulfonate (SDBS). PVBTMAC and SDBS were purchased from Polysciences Inc. (United States) and used without further purification. The oxazine dyes 9-diethylaminobenzo[a]phenoxazinone-5 (dye I) and 9-diethylaminobenzo[a]thiazinone-5 (dye II) were obtained from the Institute of

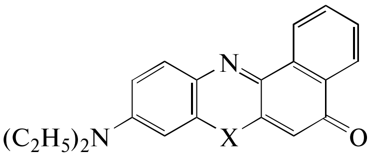
Organic Intermediates and Dyes (Russia). The structural formulas of the compounds are



(PVBTMAC)



(SDBS)



X = O (Oxazine 17)
X = S (Thiazinone)

To prepare the PVBTMAC–SDBS complex, 10 mL of an aqueous solution with concentration $c = 10^{-3}$ mol/L was first titrated using an aqueous solution of SDBS with concentration $c = 10^{-2}$ mol/L. The bend point of the conductometric titration curve corresponding to 1.24 mL of SDBS was taken as the optimum amount of surfactant required for complete precipitation. In accordance with the molar ratio [PVBTMAC] : [SDBS] = 1 : 1.24 established via conductometric titration, 31 mL of SDBS solution with a concentration of 10^{-3} mol/L was required for the quantitative precipitation of 25 mL of 10^{-3} mol/L solution. To prepare a polyelectrolyte complex in the form of a precipitate, an aqueous solution of SDBS was added drop-wise to our aqueous solution with continuous mixing for 1 h. The precipitate was then decanted five times with deionized water, followed by centrifugation at 5.5×10^3 rpm. The obtained precipitate was dried to a constant mass at room temperature and in a vacuum drying cabinet at 40°C. The yield of glass-like complex was 38%. The prepared complex was soluble in ethanol and chloroform.

The unique nature of the complex was confirmed from the absorption spectra of PVBTMAC, SDBS, and PVBTMAC–SDBS complex, recorded using a Specol 1300 spectrophotometer (Analytic Jena). The properties of monolayers were investigated in a Langmuir–Blodgett trough. The behavior of individual complex monolayers on a water surface was investigated by monitoring the dependences of surface tension π on a specific area (A) corresponding to one molecule (a π–A isotherm). A Wilhelm balance was used to measure surface tension. The rate of monolayer compression during π–A isotherm recording and the transfer of a monolayer onto a quartz glass substrate was 0.02 mm/s.

Deionized water purified with AquaMax was used as our subphase. The specific resistance of the purified water was 18.2 MΩ/cm. Surface tension was 72.8 mN/m at pH 5.6 and 22°C. The investigated layers were formed on the surface of the subphase via solution spreading. Monolayers of the polyelectrolyte–surfactant complex were investigated along with mixed monolayers based on complex and dyes. Polyelectrolyte complex and dye were dissolved separately in chloroform, followed by mixing at the ratio required for preparing a mixed monolayer. The relative concentration of dye in the investigated films was equal to 0.2, 10, 33, and 50 mol %.

The monolayers were transferred onto the glass substrate with a Y-type vertical lift at surface tension $\pi = 25$ mN/m. The number of layers in our LB films was equal to 50 at 0.2 mol % and 10 at 10, 33, and 50 mol %. The absorption spectra of LB films were recorded using a Spekol 1500 spectrophotometer (Analytik Jena); the fluorescence spectra, using a spectrofluorimeter in the photon counting mode [5].

RESULTS AND DISCUSSION

Charge Distribution in the Ground State

The distribution of electron density in the ground state was investigated for the studied compounds via the quantum-chemical method using a Pariser–Parr–Pople approximation taking into account the configuration interaction [18, 19]. Our calculations show that the maximum positive charge in the ground state of the PVBTMAC molecule was concentrated on the nitrogen atom. The highest negative charge of the surfactant molecule was located on the oxygen atom of the sulfonic group. These particular charges play an important role in the formation of polyelectrolyte-surfactant complex [20].

The maximum positive charge of the dye I molecule in the ground state is concentrated on the oxygen of the carbonyl group C=O. A high positive charge is correspondingly on the carbon of this group. The nitrogen of the pyridine ring has a considerably lower negative charge. On the other hand, this charge is sufficiently large for the six-membered cycle being not aromatic in nature. The nitrogen of the amino group carries a slight positive charge and its effect on the condensed six-membered cycles is thus minimal. Electrostatic interaction between the oxygen of carbonyl group of the dye molecule and the nitrogen atom of polyelectrolyte keeps the dye I molecules at the water–air interface.

The exchange of an oxygen atom in the benzene ring of dye II with sulfur increases the positive charge of this atom in the ground state and the pyridine ring thus becomes more polar. The charges on the rest of the atoms of a dye II molecule are virtually equal to the respective charges of a dye I molecule. The availability of the positive charge on the sulfur atom in a dye II molecule lowers the degree of interaction between this dye molecule and the complex. This should in turn affect the number of dye molecules within the mixed monolayer.

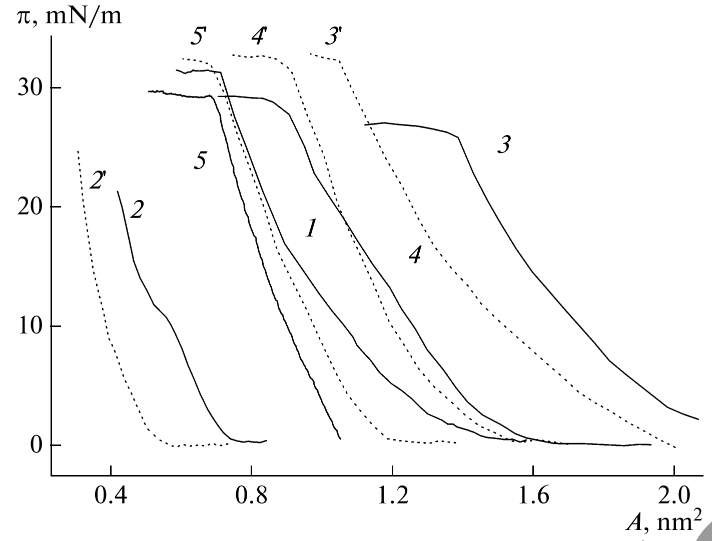


Fig. 1. Compression isotherms of monolayers of polyelectrolyte–surfactant complex (*1*) and dyes I (*2*–*5*) and II (*2'*–*5'*) at different dye concentrations: (*1*) 0, (*2*, *2'*) 100, (*3*, *3'*) 10, (*4*, *4'*) 33, and (*5*, *5'*) 50 mol %.

Phase States of the Monolayers of Polyelectrolyte–Surfactant and Polyelectrolyte–Surfactant-Dye at a Water–Air Interface

Compression isotherms of monolayers of the PVBTMAC-SDBS complex and complex-dye on the water-air interface are presented in Fig. 1. The compression isotherm of the PVBTMAC–SDBS complex is characteristic for the liquid state [21] (curve *1*). Monolayer collapse was observed at the surface tension of 31 mN/m with the specific molecular area of 0.95 nm². It was found with computer modeling of the spatial conformation of the monomeric unit that when the planes of the benzene ring of polymer and surfactant are located parallel to the water surface, the specific area A equals to 0.92 ± 0.05 nm² and the hydrophobic fragment of the molecules is located at the angle of ≈85° to the water surface. The spatial conformation of the monomeric unit of polyelectrolyte was calculated with an MM+ method on the basis of geometric sizes of molecules.

Dye molecules do not form stable monolayers (Fig. 1, curves *2*, *2'*). Curve extrapolation to the zero π value shows that the average area per one dye molecule at the tension of 20 mN/m equals $A = 0.54 \pm 0.05$ nm² and $A = 0.40 \pm 0.05$ nm² for dye I and dye II, respectively. Both values are in good agreement with the calculated cross section area of the dye molecules (0.58 and 0.43 nm²) [22]. It can be concluded on the basis of the obtained data that for the majority of the dye I molecules the plane of the central nucleolus is oriented parallel to the water surface. The dye II molecules are oriented with the short axis along the water surface.

Two-component monolayers of the polyelectrolyte complex and the dye form films with different density depending on the dye content. The collapse tension is close to the collapse tension of the complex monolayer. The isotherm shape does not change with the increase of the dye concentration. Noticeable shift of isotherms towards the lower molecular areas occurs in the process, which indicates a more compact packing of dye molecules and complex within the monolayer.

Spectral and Fluorescent Properties of Langmuir–Blodgett Films

Absorption spectra of our polyelectrolyte–surfactant complex and its individual components are presented in Fig. 2. The asorption spectrum of the PVBTMAC–SDBS complex is a combination of optical density curves of individual components (Fig. 2). The formation of LB films from the pure complex was confirmed by recording absorption spectrum of the films in the UV range. The absorption bands with maxima at 200, 225, and 260 nm are observed in the spectrum (Fig. 3). These bands are due to the benzene rings in the complex composition. The optical density increases as the number of layers grows.

Absorption and fluorescence spectra of ethanol solutions and LB films of polyelectrolyte complex–dye II are presented in Fig. 4. The absorption spectra of LB films (curves *2*–*4*) consist of wide, poorly defined bands with maxima at 570 nm, close to the absorption maximum of an ethanol solution of dye II ($\lambda_{\max}^{\text{abs}}$ = 575 nm, $\varepsilon_{\max} = 2.8 \times 10^{-4}$ M^{-1} cm^{-1}). An increase in the optical density of the dye absorption band is observed with increasing of concentration of dye molecules.

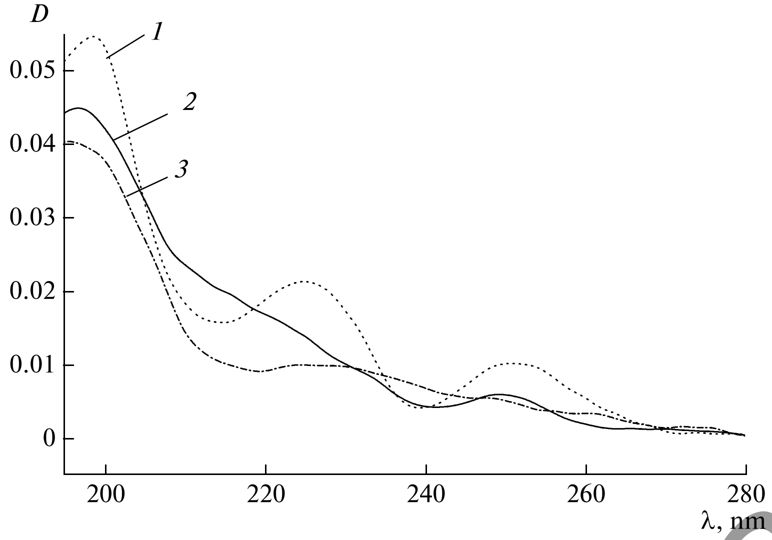


Fig. 2. Absorption spectra of solutions of polyelectrolyte complex PVBTMAC–SDBS (*1*) and SDBS (*2*) in chloroform and PVBTMAC in ethanol (*3*) at $c = 10^{-4}$ mol/L.

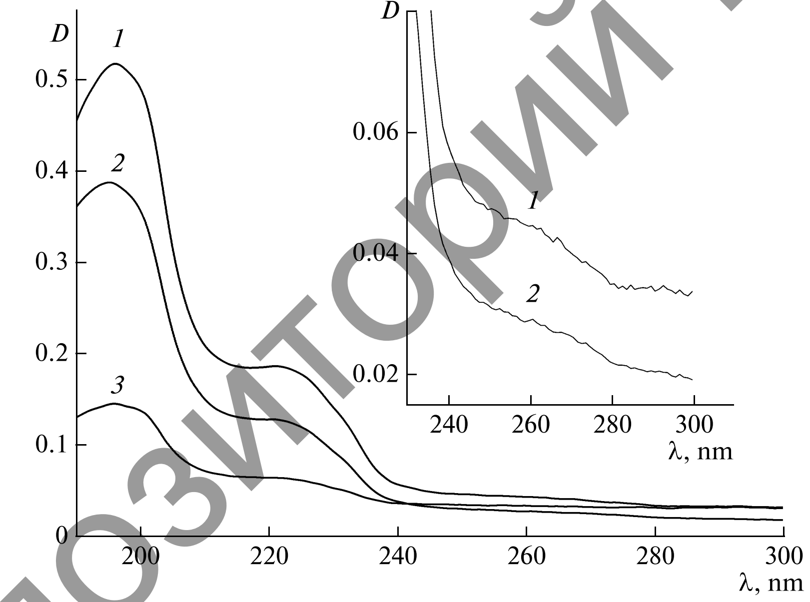


Fig. 3. Absorption spectra of LB films of PVBTMAC–SDBS at different number of layers in the film: (*1*) 30, (*2*) 20, and (*3*) 10 monolayers. The band with its maximum at 260 nm is presented in the inset.

The fluorescence spectra of LB films (curves *2'*–*4'*) were recorded upon sample excitation at λ =560 nm. A band with a maximum at 656 nm is observed for the film with $c_{\text{dye}} = 10$ mol %, which is the closest to the observed fluorescence spectrum of the alcohol solution with $\lambda^{\text{fl}}_{\text{max}} = 650$ nm (curve *1'*). The fluorescence spectra shift hypsochromically upon an increase in the concentration of dye molecules in the monolayer. The maximum of the fluorescence spectrum of the LB film with a concentration of 33 mol % lies at 650 nm, and at 634 nm for the film with a dye concentration of 50 mol %.

The spectral-luminescent properties of dye I were investigated in [23]. The maxima of the absorption and fluorescence spectra of dye I in ethanol solution lay at $\lambda^{\text{abs}}_{\text{max}} = 555$ nm ($\varepsilon_{\text{max}} = 4.2 \times 10^{-4}$ M^{-1} cm^{-1}) and $\lambda^{\text{fl}}_{\text{max}} =$ 640 nm. The absorption and fluorescence spectra of the mixed LB films of dye I and polyelectrolyte complex with luminophore concentrations of 0.2, 10, 33, and 50 mol % are presented in Fig. 5. The maximum

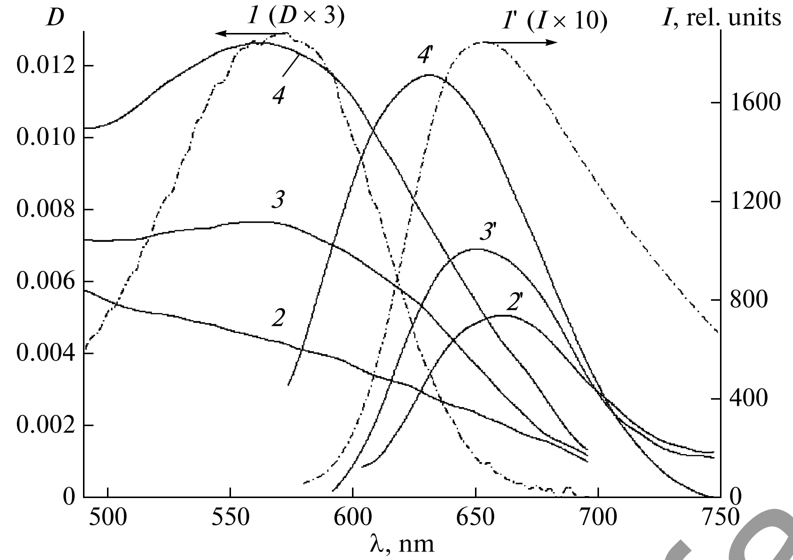


Fig. 4. Absorption (*1–4*) and fluorescence (*1'–4'*) spectra of ethanol solutions (*1*, *1'*) and LB films of polyelectrolyte complex and dye II at different dye concentrations: (*2*, *2'*) 10; (*3*, *3'*) 33; (*4*, *4'*) 50 mol %.

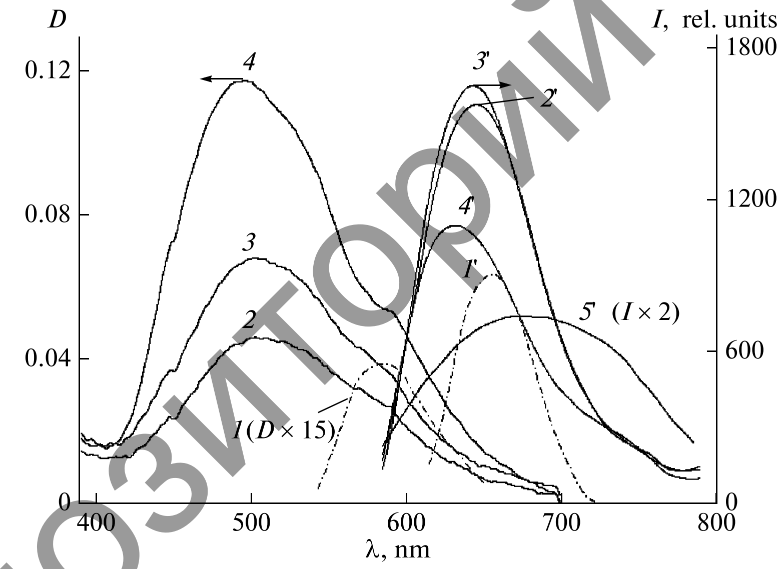


Fig. 5. Absorption (*1–4*) and fluorescence (*1'–5'*) spectra of ethanol solutions (*1*, *1'*) and LB films of polyelectrolyte complex and dye I at different dye concentrations: (*1*, *1'*) 0.2; (*2*, *2'*) 10; (*3*, *3'*) 33, (*4*, *4'*, *5'*) 50 mol %. The *5'* spectrum was excited at 490 nm.

of the absorption band of the LB film with a dye concentration of 0.2 mol % lies at $\lambda_{\max}^{\mathrm{abs}} = 590$ nm. Two absorption bands were observed for the rest of the LB films. The least intense band, observed as a shoulder on the absorption curve, lay at 590 nm for all dye concentrations. The maximum of the more intense band lay at 512 nm for a dye concentration of 10 mol %. A hypsochromic shift of the absorption maxima of the short wavelength band is commonly observed upon an increase in the dye molecule concentration, while no shift is observed for the maximum at 590 nm. The ratio of the optical density of the long wavelength band to the short diminishes slightly upon an increase in the concentration of dye in an LB film.

The fluorescence excitation of the polyelectrolyte complex and dye I LB films was performed at 570 nm. The highest emission intensity was observed for all films upon excitation in the long wavelength part of the spectrum. The maximum of the fluorescence spectrum of the film with a dye concentration of 0.2 mol % lay at 655 nm. The fluorescence spectra of the films containing 10, 33, and 50 mol % dye are shifted to the short wavelength region. The maximum intensity was observed at 648, 645, and 640 nm, respectively.

It is known that oxazine dye molecules are extremely sensitive to environment polarity due to nonrigid attachment of the electron–donor diethylamino group to the rigid aromatic fragment, which manifests as the solvatochromic effect of the absorption and fluorescence spectra of the dye. The position of the observed absorption and fluorescence spectra of the LB films indicates that the oxazine dye molecules are in a different polar environment than an alcohol solution. The short wavelength shifts of the fluorescence maxima of LB films upon an increase in dye concentration indicate a drop in the polarity of the emission center environment. This agrees with the conclusions in [24], where the increased Stokes shift of the absorption and fluorescence spectra of Nile Red was related to an increase in the environment's polarity. We may suggest that the increased density of the dye molecules results in the partial neutralization of polarity created by polyelectrolyte molecules surrounding the fluorescence centers.

The fluorescence spectra of the films with 10 and 33 mol % of dye I have fluorescence maxima at 655 nm upon excitation at 490 nm, and the fluorescence band of the film with a dye concentration of 50 mol % is widened and shifted to the red region of the spectrum with $\lambda_{\max}^{\text{fl}} = 688$ nm. The increased dye concentration in the film results in fluorescence quenching. The highest fluorescence quantum yield of the LB films is observed at a dye concentration of 33 mol %.

The observed features are in good agreement with exciton model of molecular aggregates. According to the theory of molecular aggregates [25], the exciton zone of a dimer consists of two discrete levels S_1^h (upper) and S_1^1 (lower). The absorption of dimers is not observed at a 0.2 mol % dye concentration in the film, and the formation of the absorption spectrum is due to the $S_0 \rightarrow S_1$ transition. The fraction of dimers grows with an increase in dye concentration, resulting in the emergence of a short wavelength absorption band (the $S_0 \rightarrow S_1^h$ transition).

Predominantly monomeric centers emit at an excitation at 590 nm ($S_0 \rightarrow S_1$ transition) with a maximum at 600 nm. An emission band is observed upon excitation at 490 nm, corresponding to the long wavelength transition ($S_1^1 \rightarrow S_0$). This indicates fast non-radiative relaxation from the upper S_1^h to the lower S_1^1 sublevel of the split excited state of the dimer [23].

It can be seen from Figs. 4 and 5 that the optical densities of LB films of the dye II are one order of magnitude lower than those of dye I when the number of layers and the concentration of dye molecules in the monolayers are equal. The amount of polyelectrolyte complex was identical in both cases, as was shown by the equal optical density of polyelectrolytes on the UV absorption band. This confirms the suggestion that the availability of a positive charge on the sulfur atom in the thiazone molecule lowers the degree of electrostatic interaction between the dye molecules and complex. As a consequence, fewer luminophore molecules are transferred into the LB layer than in the case of dye I.

CONCLUSIONS

Our investigation showed that the electrostatic interaction of dyes with polyelectrolyte-surfactant complex could be used for preparing luminescent Langmuir–Blodgett films based on the nonamphiphilic molecules of organic dyes. Analysis of the spectral data and the charge distribution in the ground electronic state of the dyes reveals that the degree of electrostatic interaction between the dye II molecules and polyelectrolyte complex is less than in the case of dye I. The position of the observed absorption and fluorescence spectra of LB films suggests that the oxazine dye molecules are in a polar environment in the polyelectrolyte complex. The lowered dye molecule concentration reduces the Stokes shift of the absorption and fluorescence spectra. We may suggest that an increase of the number of dye molecules reduces the effect of the polar environment on the fluorescent molecules. The stronger electrostatic interaction between the dye I molecules and the polyelectrolyte complex results in the formation of dimers of dye molecules in the monolayer.

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