

Fluorescing Behavior of Thin Solid Films Based on Polyelectrolyte-Surfactant Complex and Dye Molecules

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ABSTRACT: This article is devoted to investigation of interaction between polycomplex and dye molecules assembled in fluorescent thin solid Langmuir-Blodgett (LB) films. Preparation procedure of organosoluble stoichiometric polycomplex based on cationic polyelectrolyte and anionic surfactant is described. Formation of mixed monolayers consisting of polyelectrolyte-surfactant complex (PSC) and dye molecules—Nile Red (NR) at water-air interface is shown. Assembling conditions of LB films based on PSC and NR are defined and the spectral-luminescent properties of obtained films are studied. It is shown that when nonamphiphilic NR and PSC are mixed the excellent monolayers formed, which can easily be transferred onto solid substrates by Langmuir-Blodgett method with a high transfer coefficient. Absorption and fluorescence spectra of mixed LB films reveal the formation of dimers and existence of monomers in LB films. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 289–295, 2013

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INTRODUCTION

Polyelectrolyte-surfactant complexes (PSCs) are a new class of materials that possess supramolecular structure at the molecular level.^{1–3} Preparation, conformational, and physical-chemical properties of PSCs have been reviewed in Refs. 4 and 5.

The Langmuir-Blodgett (LB) technique is one of the effective tools to design functional nanomaterials. In particular, the typical LB compatible materials are amphiphilic molecules or mixture of nonamphiphilic molecules with fatty acids because behavior of nonamphiphilic molecules in LB films is similar to their amphiphilic precursors.^{6,7} This fact encourages studying of mixed LB films, inasmuch as such films can easily be prepared from existing nonamphiphilic molecules without chemical synthesis of amphiphilic luminophores.^{6–9}

Assembling of nanostructured LB films with the help of electrostatic interactions has advantages over a time-consuming and expensive chemical synthesis. The structure of resulting systems is reversible and stimuli-responsive to the environment change (e.g., nature of solvent, concentration of components, pH medium, temperature, etc).^{10–12} Nanostructured materials obtained by using different principles of self-organization and molecular recognition serve as a basis for the development of tunable nano-

porous materials with anisotropic properties, such as proton conductivity.^{13–15} However, despite a great number of publications devoted to study of adsorbed films and Langmuir monolayers information on fluorescent thin solid films assembled with participation of PSCs and dyes to our best knowledge is lacking.^{16,17}

Dye NR is widely used as an active material for light-emitting diodes and lasers,^{18,19} in solar energy concentrators,²⁰ sensor of the medium polarity.^{21,22}

Earlier photophysical properties of LB films based on both non-amphiphilic NR and fatty acids and its amphiphilic analog were studied. However, LB films on the basis of NR and PSC were not considered.^{23,24}

In this article, preparation procedure of organosoluble stoichiometric PSC is described. The conditions of formation of stable monolayers of PSC and their behavior were investigated at water-air interface. Method of formation of fluorescing nanodimensional solid films based on PSC and dye NR by LB technique is suggested and their spectral and fluorescence features are discussed.

EXPERIMENTAL

Stoichiometric PSC was derived from cationic polyelectrolyte—poly(*N*-vinylbenzyl-*N,N,N*-trimethylammonium chloride) (PVBT

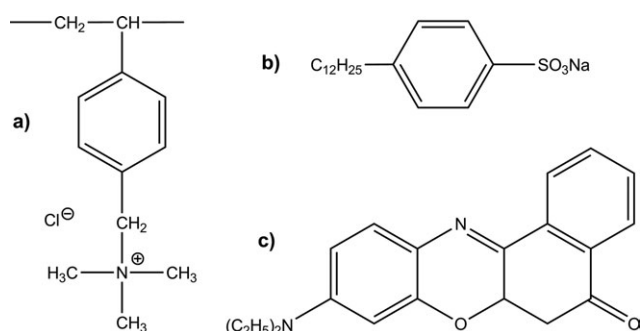


Figure 1. Structural formulae of PVBTMAC (a), DBSS (b), and NR (c).

MAC) with molecular weight $M = 2.47 \times 10^4$ and anionic surfactant—sodium salt of dodecylbenzenesulfonate (DBSS). PVBTMAC and DBSS were purchased from Polysciences Inc. (Warrington, PA, USA) and used without additional purification. Dye NR was purchased from Organic Intermediates and Dyes Institute (NIOPIK, Russia). Structural formulas of used compounds are shown in Figure 1.

Polycomplex PVBTMAC-DBSS was prepared as follows: 10 mL aqueous solution of PVBTMAC with concentration $C = 10^{-3}$ mol L $^{-1}$ was preliminarily titrated by aqueous solution of DBSS with concentration $C = 10^{-2}$ mol L $^{-1}$. Inflection point of conductometric titration curve that was equal to 1.24 mL of DBSS was taken as optimal amount DBSS that is necessary for full precipitation of PVBTMAC. On the basis of specified molar ratio of [PVBTMAC]:[DBSS] = 1:1.24 mol/mol, it was found that for quantitative precipitation of 25 mL of polyelectrolyte solution with concentration 10^{-3} mol L $^{-1}$ 31 mL of DBSS solution with concentration $C = 10^{-3}$ mol L $^{-1}$ is needed. For preparation of polycomplex as precipitate, an aqueous solution of DBSS was dropwisely added to aqueous solution of PVBTMAC during 1 h under stirring. After the precipitate was decanted by deionized water five times and finally centrifuged at 5.5×10^3 rpm. Precipitate was then dried in vacuum oven at 40°C till the constant mass. The yield

of precipitate was equal to 38%. Prepared polycomplex was soluble in ethanol and chloroform.

The properties of monolayers were studied in LB through, which was assembled in Scientific Center “NIOPIK” (Moscow, Russia). Behavior of monolayers was studied by measuring the dependence of surface pressure-specific molecular area (π -A-isotherm). Surface pressure at the air–water interface was registered with the help of a Wilhelmy balance. The compression rate of the monolayers in the course of measuring of π -A isotherm and transferring of monolayer onto solid substrates from quartz glass was 0.02 mm s $^{-1}$.

The deionized water was cleaned by AquaMax and was used as subphase. The resistivity of the deionized water was 18.2 M Ω cm $^{-1}$. The surface tension of water was equal to 72.8 mN m $^{-1}$ at pH = 5.6 and temperature 22°C.

Both monolayers of pure PSC and mixed monolayers of PSC and dye NR were studied. For preparation of mixed monolayers, the PSC and dye molecules were dissolved separately in chloroform and then mixed. Monolayers were deposited on the subphase surface by spreading of 0.2 mL of pure or mixed solution. The relative concentrations of dye molecules in mixed films were equal to 0.2; 10; 33; and 50 mol %.

Monolayers were transferred onto quartz substrates by vertical dipping according to Y-type transfer (transfer during downward and upward stroke) at pressure $\pi = 25$ mN m $^{-1}$. The number of layers in LB films was equal to 50 (0.2 mol %) and 10 layers (10, 33 and 50 mol %). The average transfer coefficient was almost identical and equal to 0.97 during downward and upward stroke for both pure PSC and mixed PSC-NR monolayers.

Absorption spectra of organic solutions (with concentrations equal to 10^{-4} mol L $^{-1}$) of PSC, polyelectrolyte, surfactant, and obtained LB films were measured on Spekol 1300 spectrophotometer (Analytik Jena). The slits of spectrophotometer were 2 nm. Fluorescence spectra of LB films were measured on a spectrofluorimeter with detection in the photon-counting mode.⁸ Excitation of fluorescence spectra of LB films based on PSC and NR was carried out with halogen lamp and monochromator.

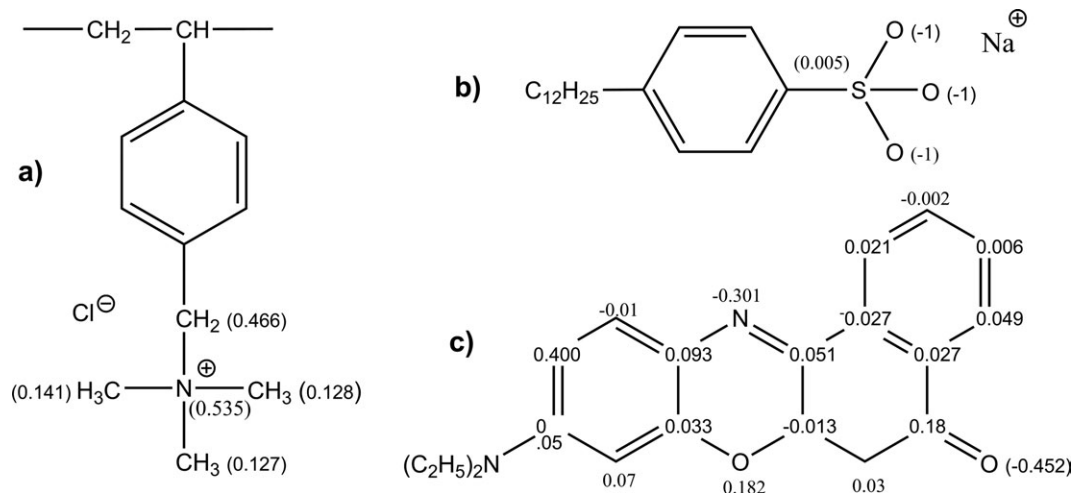


Figure 2. Calculated distribution of electronic density of PVBTMAC (a), DBSS (b), and NR (c).

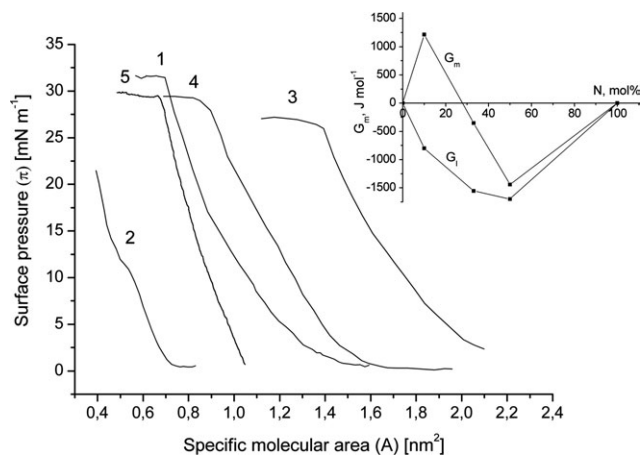


Figure 3. π -A-isotherms of PSC and NR at different concentrations of dye molecules (mol %): 1–0; 2–100; 3–10; 4–33; 5–50. The Gibbs free energy of mixed monolayers (G_M) and the curve of ideal mixing (G_I) are shown in the inset.

RESULTS AND DISCUSSION

Charge Distribution in the Ground Electronic State

Distribution of electronic density of studied compounds was investigated by quantum-chemical method in the approximation of Pariser-Parr-Pople taking into account the configuration interactions.²⁵ The calculations showed (Figure 2) that the maximum positive charge in the ground state of molecule PVBTMAC is concentrated on the nitrogen atom. The biggest negative charge of surfactant molecules is located on the oxygen atoms of sulfonic group. These charges participate in formation of PSC. The main driving force in formation of PSC is electrostatic attraction between oppositely charged units of macromolecules and surfactant ions.^{4,26}

In the ground state, the maximum negative charge of NR is concentrated on the oxygen of the carbonyl group C=O. Accordingly, a large positive charge is accumulated on carbon atoms of this group. Much smaller negative charge has the nitrogen of pyridine ring. Conversely, this charge is sufficiently large for six-membered ring to have aromatic character. Amino nitrogen has a small positive charge, and hence its effect on the condensed six-membered rings will be minimal. We suppose that ion-dipole interaction between the oxygen of the carbonyl group of the dye molecule and positive nitrogen atom of polyelectrolyte molecules will be responsible for retaining the NR at water–air interface.

Phase States of PSC and PSC-NR Monolayers at Water–Air Interface

Comprehensive information on phase state of monolayers can be obtained from π -A-isotherms. Phase state is attributed to degree of freedom of molecules in the monolayer under its compression. Phase states of monolayers depend on Van der Waals forces and intermolecular interactions between polar groups of molecules.^{27,28}

To maintain the required density of individual and mixed monolayers in the course of their transfer onto solid substrate, the stability of films was studied by two approaches.²⁹ In the first case, the changing of surface pressure was fixed at constant area of monolayer during 150 min. For all monolayers, a significant change of surface pressure was observed during 60 min.

The value of the surface pressure decreased two times during 60 min in comparison with value of π , which was registered after 20 min when the solvent evaporation takes place. Next 90 min surface pressure did not change essentially.

In the second case, the change of monolayer area (ΔS) was fixed at constant surface pressure ($\pi = 22 \text{ mN m}^{-1}$) during 90 min. Monolayer occupied constant area after 70 min; the significant values of ΔS were fixed during 20 min due to solvent evaporation. It should be noted that stabilization of monolayer of pure dye did not occur even after 180 min. Compression isotherms of monolayers of PVBTMAC-DBSS complex and monolayers of PSC-NR are shown in Figure 3.

The shape of π -A-isotherm of PVBTMAC-DBSS polycomplex is typical for liquid state (Figure 3, curve 1).²⁷ Collapse of monolayer with specific molecular area of 0.95 nm^2 was observed at surface pressure of 31 mN m^{-1} . The spatial conformation of the monomer unit of PSC was modeled by the MM+ force field method. It was found that if the plane of the benzene fragments of polymer and surfactant is located in parallel to water surface the specific area A is equal to $0.92 \pm 0.05 \text{ nm}^2$ while the hydrophobic fragment of the molecule is located at the angle approximately 85 degrees to the plane of water surface.

It is known that for nonamphiphilic dyes that are insoluble in water, e.g., for oxazines dyes, it is possible to record an isotherm of monolayer compression on phase interface.³⁰ Monolayers of nonamphiphilic molecules are instable and cannot be transferred onto solid substrates.^{6,30}

It was observed (Figure 3, curve 2) that pure NR at the air–water interface does not form stable monolayer and surface pressure rise from an initial “zero” value to about 20 mN m^{-1} . Extrapolation of curve 2 to zero value of π gives the estimated average area of one dye molecule $A = 0.54 \pm 0.05 \text{ nm}^2$ at pressure 20 mN m^{-1} . This value is in good agreement with cross-sectional area of aromatic fragment along long axis of molecule (0.58 nm^2) calculated on the basis of geometry of NR molecule in vacuum.²⁴ Earlier²⁴ the analogue of the amphiphilic NR molecules–oxazine 41 was studied. Calculated average area of one dye molecule of oxazine 41 was found to be $A = 0.5583 \text{ nm}^2$. Observed small differences in the cross-sectional area of the molecules found in our work and in Ref. 24 may be explained as follows. The aromatic moiety of the molecule of oxazine 41 due to hydrophobic tail, is likely oriented at an angle to the plane of the water. This will give some low value of the specific molecular area of the dye in the monolayer. In the course of estimation of cross-sectional area of the molecule of non-amphiphilic NR by MM+ it was concluded that for these molecules the molecular plane is parallel to the water surface. Therefore the cross-sectional area of the molecules of NR which was found in our work is bigger than in Ref. 24.

The π -A isotherms of mixed monolayer PSC-NR are identical to the shape of PVBTMAC-DBSS isotherm. The value of collapse pressure of mixed monolayer is close to collapse pressure of PSC monolayer. It is evidence from the Figure 3, the monolayer with dye concentration equal to 10 mol % (curve 3) collapses at 26 mN m^{-1} , and area of molecules within monolayer at $\pi = 25 \text{ mN m}^{-1}$ (pressure of transfer of monolayer onto solid substrate) is equal to 1.6 nm^2 . The shape of isotherms

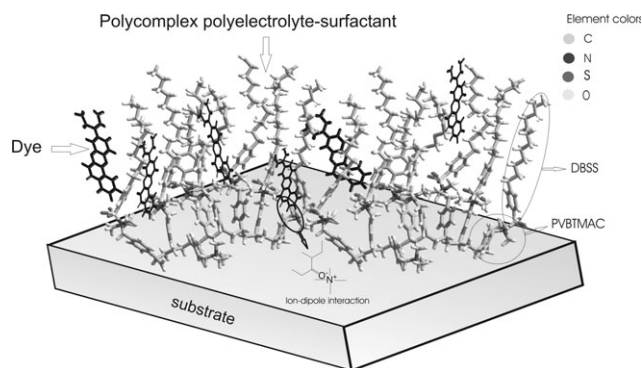


Figure 4. Schematic representation of polyelectrolyte-surfactant/dye layer deposited onto solid substrate.

does not change with growth of dye concentration, the collapse pressure increases up to 28 mN m^{-1} . The appreciable shift of isotherm to the smaller molecular areas occurs, indicating a more compact packing of dye molecules and PSC within the monolayer. In particular, the specific molecular area for monolayers containing 33 and 50 mol % of NR is equal to 1.38 and 1.0 nm^2 respectively. Taking into account the adsorption behavior of PSC at silica surface,^{31,32} one can suppose that the dye molecules are dipped within DBSS environment of PSC as a result of hydrophobic interactions (Figure 4).

To evaluate intermolecular interaction between dye molecules and PVBtMAC-DBSS and dye in monolayers as well as thermodynamic stability of the system, the Gibbs free energy was calculated. The increment of free Gibbs energy was evaluated from the π -A-isotherm by the following equations^{6,33}:

$$G_I = RTN_1(\ln N_1) + RTN_2(\ln N_2), \quad (1)$$

$$\Delta G_E = \int_0^\pi (A_{12} - N_1 A_1 - N_2 A_2) d\pi, \quad (2)$$

$$G_M = G_I + \Delta G_E, \quad (3)$$

where ΔG_E is the excess free energy of mixing, G_I is the free energy of mixing for an ideal system, G_M is the free energy of

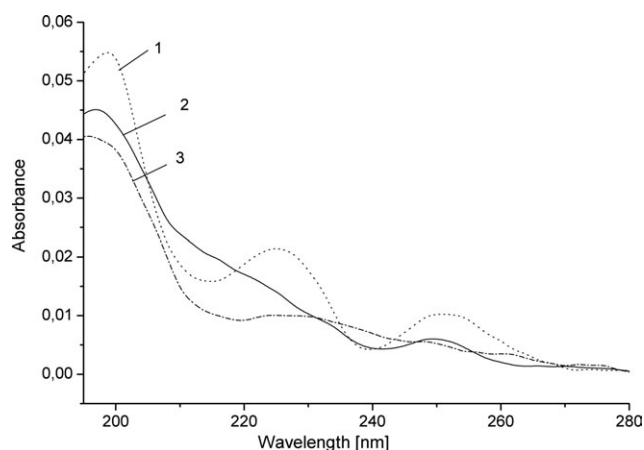


Figure 5. Absorption spectra of solutions of polycomplex PVBtMAC-DBSS (1) and DBSS (2) in chloroform and PVBtMAC in ethanol (3).

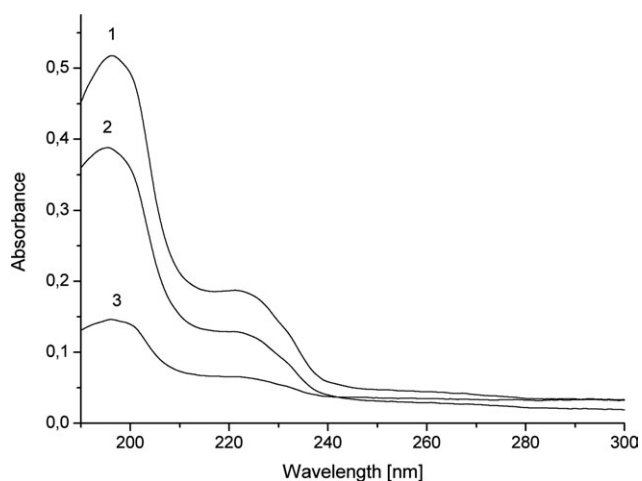


Figure 6. Absorption spectra of LB films of PVBtMAC-DBSS at different number of layers in the film: 1–30; 2–20; and 3–10 monolayers.

mixing; A_1 , A_2 , and A_{12} are the corresponding areas of molecules in the monolayers of dye, pure PSC, and mixed PSC-NR monolayer correspondingly; N_1 and N_2 are the molar fractions of dye and PSC, correspondingly. R is the universal gas constant, π is the surface pressure taken from the isotherms, and T is the temperature in Kelvin. The increment of free energy of mixing was evaluated for $\pi = 0$ – 21 mN m^{-1} .

Plots of the Gibbs free energy of mixing (G_M) versus the mole fraction of NR in the mixed monolayer are shown in the inset of Figure 3. One can see that the value of G_M deviates from zero at all ratio of PSC-NR mixture. It demonstrates the immiscibility of components in monolayer.^{6,27} The values of $G_M > 0$ at minimal content of dye molecules within the monolayer (10 mol %) confirm energetically unfavorable interaction. According to the π -A isotherm, the specific molecular area for a given concentration is equal to total area of individual dye molecules and monomer units of PSC. Since under these conditions the monolayer consists of mainly macromolecules of PSC, we can assume that the repulsive forces between similar molecules are dominant in the monolayer. In this case, the phase separation of the components in the mixture of dye-PSC into clusters or aggregates can take place. Formation of such clusters and simple crystalline domains was reported both for nonamphiphilic and surface-active molecules.^{6,34} The values of $G_M > 0$ at minimal content of dye molecules within the monolayer (10 mol %) confirm energetically unfavorable interaction. According to the π -A isotherm, the specific molecular area for a given concentration is equal to total area of individual dye molecules and monomer units of PSC. When the dye concentration is higher than 10 mol %, the $G_M < 0$. The negative values of the increment of Gibbs energy indicate that the degree of interaction between dye molecules and PVBtMAC increases.³³ The area per molecule becomes close to the area of the monomer unit of PSC. It gives evidence of close packing of dye molecules and PSC within the monolayer.

Spectral-Fluorescent Properties of LB Films

Absorption spectra of PSC, PVBtMAC, and DBSS in organic solvents were recorded (Figure 5). It is seen that the absorption

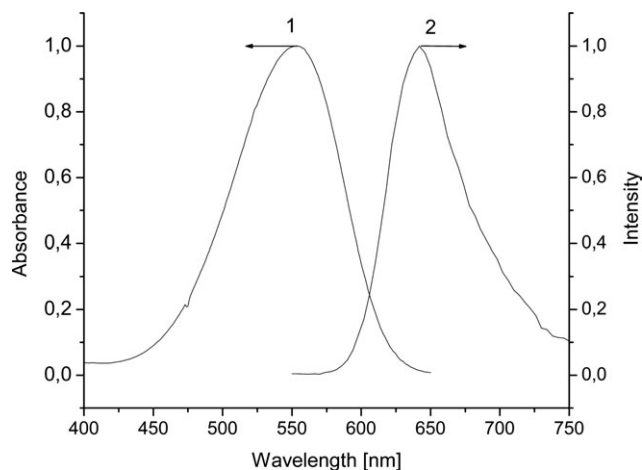


Figure 7. Absorption (1) and fluorescence spectra (2) of NR in ethanol solution at concentration $C = 10^{-5}$ mol L⁻¹.

spectrum of PVBTMAC-DBSS complex represents a combination of optical density curves of individual components.

The formation of LB films from the pure PSC was confirmed by measuring the electronic absorption spectra of films in the UV region. Two absorption bands with the maxima at 195 and 225 nm were observed (Figure 6). Absorption spectrum correlates well with absorption spectrum of PSC in solution. The optical density of films increases with increasing of number of layers.

Figure 7 shows the absorption spectra and fluorescence spectra of NR in ethanol solution. Absorption and fluorescence spectrum of NR exhibits the maximum at $\lambda_{\text{max}}^{\text{abs}} = 550$ nm and $\lambda_{\text{max}}^{\text{fl}} = 640$ nm, correspondingly.

Absorption and fluorescence spectra of mixed LB films of PSC and NR are shown in Figure 8. Absorption band of LB film with concentration of dye 0.2 mol % exhibits the maximum at $\lambda_{\text{max}}^{\text{abs}} = 590$ nm (Figure 8, curve 1). This band is red shifted in comparison with the absorption spectrum of NR ethanol solu-

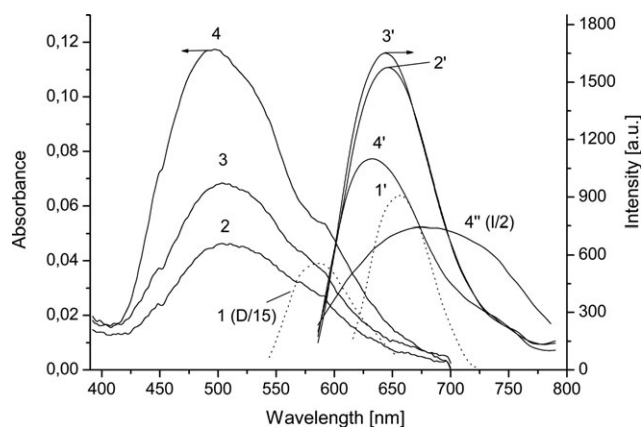


Figure 8. Absorption (1–4) and fluorescence (1'–4' at $\lambda_{\text{ex}} = 570$ nm) (4'' at $\lambda_{\text{ex}} = 490$ nm) spectra of LB films of PSC and NR at different concentration of dye (in mol %): 1,1'–0.2; 2,2'–10; 3,3'–33; 4,4',4''–50.

Table I. Parameters of Absorption ($\lambda_{\text{max}}^{\text{abs}}$) and Fluorescence ($\lambda_{\text{max}}^{\text{fl}}$) Spectra of LB Films of PSC-NR

Dye concentration, mol %	$\lambda_{\text{max}}^{\text{abs}}$, nm	$D_{\text{lw}}/D_{\text{shw}}$	$\lambda_{\text{max}}^{\text{fl}}$, nm	
			$\lambda_{\text{ex}} = 490$	$\lambda_{\text{ex}} = 590$
0.2	590	–	660	660
10	512	0.59	655	648
33	508	0.53	655	645
50	496	0.45	688	640

tion. Short-wave absorption band with the maximum at 490–512 nm appears (Figure 8, curves 2–4) in addition to monomeric band with a maximum at 590 nm with increasing of dye concentration in film. The intensity of the short-wave absorption band is much higher than that of the monomer and increases with increasing of concentration. The ratio of optical densities at 590 nm to short-wavelength maximum band decreases with increasing of dye concentration in the LB film (Table I).

Maximum of the fluorescence spectrum of film with concentration of dye 0.2 mol % was observed at 660 nm at excitation at $\lambda_{\text{ex}} = 590$ nm (Figure 8, curve 1'). Fluorescence spectra of films containing 10, 33, and 50 mol % of dye molecules are weakly shifted to short-wavelength region (Figure 8, curves 2'–4'). The fluorescence intensity increases for concentrations of 10 and 33 mol %. For dye concentration of 50 mol %, a quenching of fluorescence is observed (Figure 8, curve 4'). Red-shifted low-intensity fluorescence band is observed under excitation with wavelength at 490 nm. Spectrum of this fluorescence is shown on Figure 8 (curve 4'').

Observed absorption and fluorescence spectrum of NR LB films is well described by exciton model of molecular aggregates.³⁵ According to this model, the interaction of monomeric dye molecules in the dimer splits excited level S_1 of dimer on two sublevels S_1^h and S_1^l , one being lower (S_1^l) and other (S_1^h) being higher in energy than the corresponding monomeric singlet state (Figure 9). Probability of transitions from the ground state to one of the excited sublevels depends on the mutual position of the dipole moments of the electronic transition $S_0 \rightarrow S_1$ of the molecules in the dimer.

If the plane of the molecules, constituting the dimer, is parallel (sandwich type dimers), only one of the two possible transitions

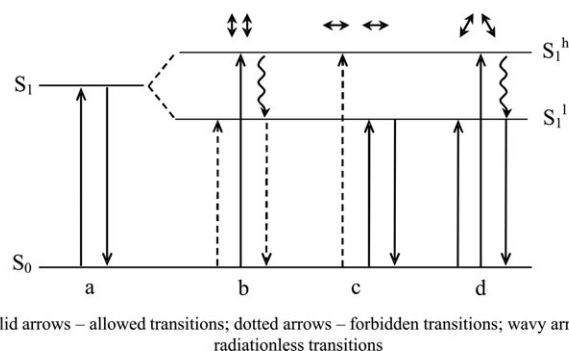


Figure 9. A scheme of energy levels of monomer (a) and dimers (b–d) of NR molecules.

is allowed ($S_0 \rightarrow S_1^h$). This transition exhibits as shortwave band in the absorption spectrum [Figure 9(b)]. If the angle between the planes of the molecules is close to 180 degrees (plane dimers), then the absorption spectrum consists only by long-wavelength band, which corresponds to the transition $S_0 \rightarrow S_1^h$ (Figure 9(c)). In the case of the angle between the plane of the molecules between 0 and 180 degrees (herringbone dimers), both transitions are allowed (Figure 9(d)).

When the dye concentration in the film is equal to 0.2 mol %, dimer formation is inefficient and the absorption spectrum of monomers dominates ($S_0 \rightarrow S_1$). The amount of sandwich dimers increases with increasing of dye concentration that leads to appearance of short-wavelength band of absorption with a maximum at 512–490 nm (transition $S_0 \rightarrow S_1^h$). The changes observed in the fluorescence spectra confirm this assumption. The monomeric centers preferentially emit at excitation 590 nm (transition $S_0 \rightarrow S_1$) with maximum of fluorescence spectrum at 660 nm. In case of excitation at 490 nm, the low-intensity band corresponding to forbidden long-wave electronic transition ($S_1^f \rightarrow S_0$) is observed.

CONCLUSIONS

Organosoluble PSC based on cationic polyelectrolyte and anionic surfactant was synthesized. The conditions of formation of stable monolayers and their behavior were investigated at water–air interface. It is shown that polyelectrolyte films can be transferred onto quartz substrates.

Method of formation of mixed monolayers polyelectrolyte-surfactant-dye was suggested. When nonamphiphilic NR and PSC are mixed, the excellent monolayers are formed, which can easily be transferred onto solid substrates by LB method with a high transfer coefficient.

In spite of a great number of publications devoted to study of adsorbed films and Langmuir monolayers of PSC to the best of our knowledge investigation of Langmuir-Blodgett films based on PCS and non-amphiphilic dye was carried out for the first time.

Spectroscopic study of obtained films shows that absorption and fluorescence spectra of mixed LB films consisting of PSC and NR in visible region are shifted in comparison with ethanol solutions. Spectral changes of mixed films reveal the formation of sandwich dimers and the existence of monomer molecules of dye in LB films. When the dye concentration in the film is small, dimer formation is inefficient and the absorption spectrum of monomers dominates. The amount of sandwich dimers increases with increasing of dye concentration that leads to appearance of short-wavelength band of absorption.

The changes observed in the fluorescence spectra confirm this assumption. On excitation in the long-wave absorption band, the monomeric luminescence centers fluoresce predominantly. The red-shifted fluorescence spectra are obtained by excitation in the short-wave wing of the absorption spectrum. In this case, the low-intensity band corresponding to forbidden long-wave electronic transition is observed.

Our studies show that for obtaining of high quality luminescent Langmuir-Blodgett films, the electrostatic interaction of PSC and nonamphiphilic organic dye can successfully be used.

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