

Properties of Langmuir-Blodgett Films Based on Organosoluble Polyelectrolyte-Surfactant Complex and Oxazine Dye

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Preparation procedure of organosoluble stoichiometric polycomplex based on cationic polyelectrolyte and anionic surfactant has been described. It was shown the formation of mixed monolayers consisting of polyelectrolyte-surfactant complex and dye molecules at the water-air interface. Assembling conditions of fluorescent nanosized solid Langmuir-Blodgett films based on polycomplex and dye Nile Red were defined and the spectral-luminescent properties of obtained films were studied. Absorption and fluorescence spectra of mixed Langmuir-Blodgett films revealed that electrostatic interaction between polycomplex and dye molecules is responsible for formation of dimers.

Keywords: Langmuir-Blodgett films, Optical properties, Polyelectrolyte, Oxazine dye.

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1. INTRODUCTION

Polyelectrolyte-surfactant complexes are a new class of materials that possess supramolecular structure at the molecular level. Preparation, conformational and physico-chemical properties of polyelectrolyte-surfactant complexes have been reviewed in [1, 2]. Recently organosoluble stoichiometric polyelectrolyte-surfactant complexes attracted much attention of researchers [3-5].

The unique property of dye Nile Red is that it is widely used as an active material for light-emitting diodes and lasers [6, 7], in solar energy concentrators [8], sensor of the medium polarity [9, 10].

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 non-amphiphilic molecules with fatty acids because behavior of non-amphiphilic molecules in LB films is similar to their amphiphilic precursors [11, 12]. This fact encourages studying of mixed LB films, inasmuch as such films can easily be prepared from existing non-amphiphilic molecules without chemical synthesis of amphiphilic luminophores [11-14].

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., solvent quality, concentration of components, pH, temperature, etc.) [15-17]. Nanostructured materials obtained by using of different principles of self-organization and molecular recognition serve as a basis for the development of tunable nanoporous materials with anisotropic properties, such as proton conductivity [18-20]. However, in spite of a great number of publications devoted to study of adsorbed films and Langmuir monolayers [21, 22] information on fluores-

cent thin solid films assembled with participation of polyelectrolyte-surfactant polycomplexes and dyes to our best knowledge is lacking.

The main aim of the present paper is to study the fluorescing behavior of nanosized Langmuir-Blodgett films based on polyelectrolyte-surfactant complex and dye Nile Red.

2. EXPERIMENTAL

Stoichiometric polyelectrolyte-surfactant polycomplex was derived from cationic polyelectrolyte – poly(*N*-vinylbenzyl-*N,N,N*-trimethylammonium chloride (PVBTMAC) with molecular weight $M = 2.47 \cdot 10^4$ and anionic surfactant – sodium salt of dodecylbenzenesulfonate (DBSS). PVBTMAC and DBSS were purchased from Polysciences Inc. (USA) and used without additional purification. Dye Nile Red was purchased from Organic Intermediates and Dyes Institute (Russia). Structural formulas of used compounds are shown in Fig. 1.

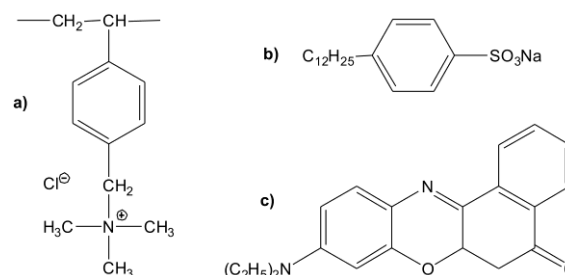


Fig. 1 – Structural formulas of (a) PVBTMAC, (b) DBSS and (c) Nile Red.

Polycomplex PVBTMAC-DBSS was prepared as follows: 10 mL aqueous solution of PVBTMAC with concentration $C = 10^{-3}$ mol/L was preliminarily titrated by aque-

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ous solution of DBSS with concentration $C = 10^{-2}$ mol/L. Inflection point of conductimetric 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 it is needed 31 mL of DBSS solution with concentration $C = 10^{-3}$ mol/L. 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 5 times and finally centrifuged at $5.5 \cdot 10^3$ rpm. Precipitate was then dried in vacuum oven at 40°C till the constant mass. The yield of glass precipitate was equal to 38 %. Prepared polycomplex was soluble in ethanol and chloroform.

The individuality of polycomplex was confirmed by absorption spectroscopy

The properties of monolayers were studied in Langmuir-Blodgett through. 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 that allows to detect the surface tension in the range of 0 to 100 mN/m with accuracy equal to 0.1 %. 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.

The deionized water was cleaned by AquaMax and was used as subphase. The resistivity of the deionized water was 18.2 M Ω /cm. The surface tension of water was equal to 72.8 mN/m at $pH = 5.6$ and temperature 22°C . Monolayers were deposited on the subphase surface by spreading of solution.

3. RESULTS AND DISCUSSION

3.1 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-People, taking into account the configuration interactions [24]. The calculations showed 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 sulfonate group. These charges play a major role in the formation of polyelectrolyte-surfactant complex [25].

For molecules of dye Nile Red in the ground state the maximum negative charge is concentrated on the oxygen of the carbonyl group C=O. Accordingly, a large positive charge is appeared on carbon atom of this group. Much smaller negative charge has the nitrogen of pyridine ring. On the other hand, this charge is sufficiently large to 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. Electrostatic interaction between the oxygen of the carbonyl group of the dye molecule and the nitrogen atom of polyelectrolyte molecules will retain the Nile Red at the water-air interface.

3.2 Spectral-fluorescent properties of Langmuir-Blodgett films

Absorption and fluorescence spectra of LB films were measured on a Spekol 1500 spectrophotometer (Analytic Jena) and a spectrofluorimeter with detection in the photon counting mode [13]. The formation of LB films from the pure polycomplex 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. They are attributed to benzene rings containing in the structure of polycomplex, e.g. PVBTMAC and DBSS. The optical density of films increases with increasing of number of layers.

Absorption and fluorescence spectra of mixed LB films of polycomplex and Nile Red are shown in Fig. 2. Absorption band of LB film with concentration of dye 0.2 mol % exhibits the maximum at $\lambda_{max} = 590$ nm. For other LB films two bands in the absorption spectra appear. The least intense band is located at 590 nm for all concentrations of the dye and appeared as a shoulder on the absorption curve.

For dye concentrations of 10 mol. % the maximum of more intensive band is observed at 512 nm. It should be noted that with increasing of concentration of dye molecules in the film the maxima of short-wave absorption bands are shifted hypsochromically. At the same time the maximum at 590 nm does not shift. The excitation of the fluorescence spectrum of mixed LB films was performed at two wavelengths – $\lambda_{ex} = 490$ and $\lambda_{ex} = 590$ nm by using of halogen lamp and monochromator. For all films the maximal intensity of luminescence was obtained at excitation of fluorescence in long wavelength wing of absorption spectrum. Maximum of the fluorescence spectrum of film with concentration of dye 0.2 mol % was observed at 655 nm. Fluorescence spectra of films containing 10, 33 and 50 mol % of dye molecules are shifted to short wavelength region. The maximal intensity corresponds to 648, 645 and 640 nm.

The fluorescence spectra of films excited at 490 nm (concentration of dye 10 and 33 mol % respectively) have a maximum at 655 nm. Fluorescence band of film containing 50 mol % dye molecules is broadened and shifted to the red spectral region with $\lambda_{max} = 688$ nm. Increasing of dye concentration in film leads to quenching of the intensity of fluorescence. The maximal value of fluorescence quantum yield for LB films was obtained at 33 mol % dye concentration.

The spectral behavior of mixed films is well described by exciton model of molecular aggregates. According to molecular aggregates theory the spectral behavior of mixed films is well described by exciton model of molecular aggregates. According to molecular aggregates theory [30], the exciton band of dimer consists of two discrete levels S_1^h and S_1^l . When dye concentration in film is equal to 0.2 mol % the absorption

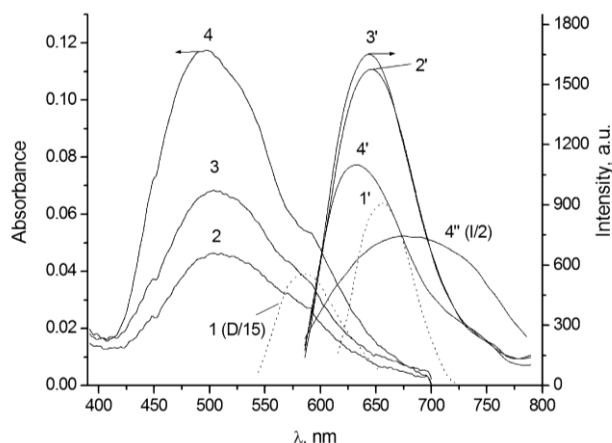


Fig. 2 – Absorption (1 – 4) and fluorescence (1'– 4' at $\lambda_{\text{ex}} = 570$ nm) (4'' at $\lambda_{\text{ex}} = 490$ nm) spectra of LB films of polycomplex and Nile Red at different concentration

of dimers is not observed and the formation of absorption spectrum of monomer is connected with transition $S_0 \rightarrow S_1$. The amount of dimers increases with increasing of dye concentration that leads to appearance of short-wavelength band of absorption (transition $S_0 \rightarrow S_1^h$).

The monomeric centers preferentially emit at excitation 590 nm (transition $S_0 \rightarrow S_1$) with maximum at

660 nm. The band corresponding to long-wave electronic transition ($S_1^l \rightarrow S_0$) is observed in case of excitation at 490 nm. This is evidence of fast nonradiative relaxation from the higher S_1^h to lower S_1^l sublevel of the splitted and excited state of dimer [30, 31].

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