

Preparation and Properties of Nanofilms Based on Polymethine Dyes by Langmuir-Blodgett Technology

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A study of physico-chemical properties of monomolecular layers of amphiphilic cationic polymethine dye - thiacyanin on the surface of the water subphase and the conditions of obtaining of Langmuir-Blodgett (LB) films are presented. The value of area, occupied by one molecule of the dye in different states of monolayer was defined. The spectral-luminescent properties of cationic polymethine dye was studied. An excimer fluorescence in LB films was revealed. It was shown, that in LB films, unlike solutions excimer not forms from monomers, but it forms from dimers of dyes. A possible mechanism of their formation was considered.

Keywords: Polymethine dyes, Langmuir-Blodgett films, Spectral properties

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1. INTRODUCTION

Currently, intensive search for new functional materials with desired optical properties for nanophotonics and optoelectronics is occurs [1, 2]. In this direction, a very promising technology is the Langmuir-Blodgett (LB) for synthesis of multimolecular systems based on optically active centers [3]. As these centers are especially promising are the polymethine dyes with higher (fatty) alkyl radicals [4], because this class of dyes has the widest range of photophysical and photochemical properties of organic dyes [5].

The aim of this work is studying of spectral properties of amphiphilic fluorescent dye in LB films in comparison with the liquid solutions and polymers, as well as the study of the phase state of dye monolayers on the surface of the water subphase, the conditions for obtaining of LB film of dye.

2. EXPERIMENT

Classical cationic polymethine (cyanine) dye thiacyanin was used.

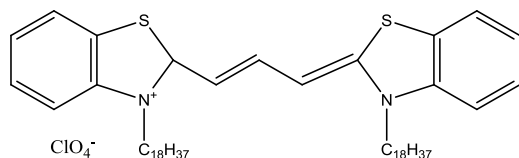


Fig. 1 – Structure of the dye

Monomolecular film were formed on the water / air interface in Langmuir bath. Bidistilled deionized water was used as subphase. The surface tension of water at a pH of 5-6 and a temperature of 20 °C was equal to 72.8 mN/m.

Bicomponent molecular monolayers of dye and stearic acid (SA) were prepared at concentrations of dye equal to 9, 17, 50 mol %. Compression isotherms of

monolayers were measured at a temperature of 20 °C. Transfer of monolayers onto nonluminescent quartz substrate by method of vertical dipping was performed at $\pi = 28$ mN/m. The speed of movement through the monolayer was 0.02 mm/s. The film thickness was equal to 20 monolayers. The films were prepared by Z type.

Spectrofluorometer Solar CM 2203 was used for measurements of absorption and fluorescence spectra. The fluorescence quantum yield was determined relative to the standard ethanol solution of rhodamine 6G.

3. RESULTS AND DISCUSSION

The spectral-luminescent characteristics of dye in ethanol, chloroform and PVB (Table) was studied. It was found that the absorption and fluorescence of the dye in liquid solvents and PVB have almost the same universal shape characteristic of organic dyes. The maxima of spectral bands slightly shifted to the red region due to the differences in the polarity of the solvents.

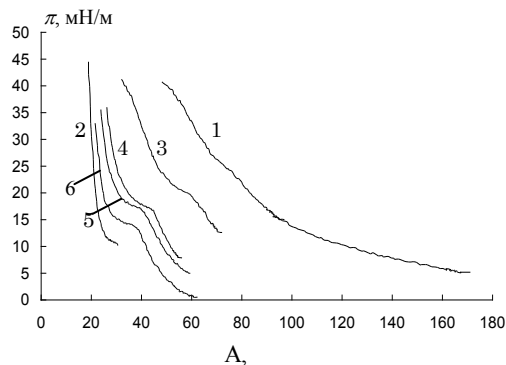
It can be seen that the dye monolayers are predominantly in the liquid state. The conformational analysis of the spatial structure of the dye molecules, made by molecular mechanics force field MM⁺, shows that the chromophore part of the molecule is almost planar structure. A slight reorientation of chromophore, at which the plane of molecule is partially out of the surface of water was found at the surface increasing.

Mixture of molecules and dye with SA form a more condensed layers with the densest packing of molecules. From the results of the calculation of miscibility of components within a monolayer, it was found that two-component dye monolayers and fatty acid are well mixed. Thus, as follows from the results of conformational analysis, stearic acid molecule is placed in the cavity formed between the fatty radical of dye molecules. Isotherms of pressure of monolayers of dye were measured (Fig. 2).

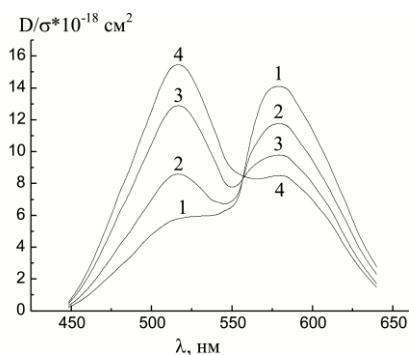
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Table 1 – Spectral-luminescent parameters of dye

| Solvent | λ_{\max}^{ab} , nm | $\Delta\tilde{\nu}_{1/2}$, cm^{-1} | $\varepsilon \times 10^{-5}$, $l \times \text{mol}^{-1} \times \text{cm}^{-1}$ | f | μ , D | λ_{\max}^f , nm | $\Delta\tilde{\nu}_{1/2}$, cm^{-1} | φ |
|------------|----------------------------|----------------------------------------------|---------------------------------------------------------------------------------|------|-----------|-------------------------|----------------------------------------------|-----------|
| Ethanol | 559 | 974 | 1,7 | 0,69 | 9,06 | 585 | 1524 | 0,07 |
| Chloroform | 568 | 927 | 2 | 0,82 | 9,92 | 595 | 1523 | 0,15 |
| PVB | 566 | 974 | – | – | – | 587 | 1700 | – |

**Fig. 2** – π -A- isotherms of monolayers of dye and SA with different concentrations of dye C_d , mol %: 1 – 100; 2 – 0; 3 – 50; 4 – 25; 5 – 17; 6 – 9

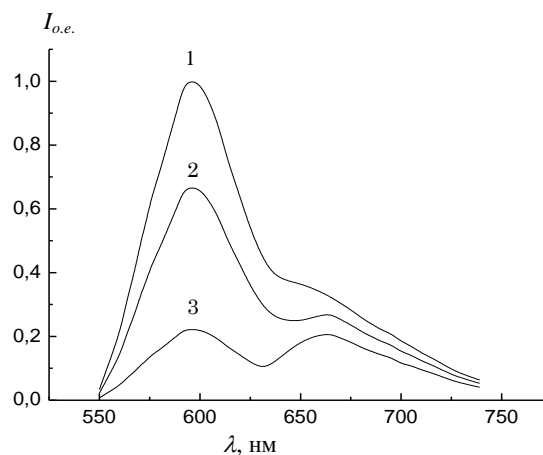
The absorption and fluorescence spectra of LB films of dye and stearic acid were measured. Measurements have shown that the absorption spectra of the dye reveals two peaks (Fig. 3). The ratio of its intensity at the increasing of dye concentrations, and long wavelength decreases. The absorption spectrum of the LB film with dye concentration of 9 mol % is similar to the absorption spectrum of the dye in chloroform. In such a film dye molecules are preferably in the form of monomers. Monomers have absorption band with maximum at $\lambda_{\max} = 580$ nm. The short wavelength band with $\lambda_{\max} = 518$ nm, observed for the films with a high concentration of dye, belongs to the molecular aggregates. To elucidate the possible packing of the dye molecules in the monolayer the conformational analysis of dimers of dyes for different conformations was performed. The results of the calculation shows that dimers of "sandwich" type are energetically favorable.

**Fig. 3** – Absorption spectrum of LB films at various concentration of dye C_d , mol %: 1 – 9; 2 – 17; 3 – 50; 4 – 100

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Two bands reveals in the fluorescence spectra of LB films of the dye upon excitation at the maximum of absorption band of the dimer (Fig. 4). More intense short-wave band with a maximum at 595 nm coincides with the position of the fluorescence band of the dye in the solution and the appropriate to the emission of monomers. The position of the maximum of broad wavelength band varies from 645 to 670 nm with increasing of dye concentration in mixed Langmuir-Blodgett films. This band has a maximum at 650 nm for the LB film of pure dye. In the mixed LB films increasing of the dye concentration leads to an increase in the ratio between the intensities of the long-wave and short-wave bands. Quantum yield of fluorescence of the films with increasing of dye concentration decreases.

**Fig. 4** – Fluorescence spectrum at various concentration of dye C_d , mol %: 1 – 9; 2 – 17; 3 – 50

These results can be explained as follows. As already indicated, in the LB films of dye along with the monomers the dimers of "sandwich" type are presented, in which the long-wave electronic transition is forbidden in the dipole approximation. As a result, dimers of this type generally do not exhibit fluorescent ability. Therefore, the long-wavelength band in the fluorescence spectrum of the dye LB films can not belong to dimers. The absence in the spectrum of absorption of these films additional bands and the presence of broad structureless fluorescence band with a large Stokes shift indicates the excimer nature of the long-wavelength emission.