SHORT COMMUNICATIONS

The Aggregation of Rhodamine Dye Molecules in Mixed Langmuir–Blodgett Films

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Abstract—Mixed Langmuir–Blodgett films based on amphiphilic rhodamine dye molecules, hydrophobically modified polyampholyte, and stearic acid were prepared. The properties of monolayers at the water–air interface were studied. Three-component monolayers were found to be in a more condensed state than two-component ones. The absorption and fluorescence spectra of the films were recorded. Molecular aggregates with various structures could be produced by varying the concentrations of dye molecules, polymer, and stearic acid.

INTRODUCTION

The spectral properties of Langmuir–Blodgett films prepared from amphiphilic rhodamine dye molecules and hydrophobically modified polyampholyte polymer were studied in [1, 2]. The absorption and fluorescence spectra of Langmuir–Blodgett films were recorded at various dye-to-polymer ratios. It was found that, because of the close packing of molecules in Langmuir–Blodgett films, effective aggregation of dye molecules occurred. The films had comparatively high thermal and mechanical strength compared with mixed films of dyes and fatty acids.

The addition of fatty acids to dye monolayers caused the formation of monolayers in a more condensed state [3], which improved the transfer of films to solid substrates. It can be expected that the addition of fatty acid molecules to a two-component dye–polymer system should fill micropores in the mixed monolayer and influence aggregation. In miscible monolayers, fatty acid molecules get built in between dye molecules and can decrease the degree of aggregation and increase the quantum yield of fluorescence of luminophors in Langmuir–Blodgett films. With immiscible monolayers, a cluster structure with a still closer packing of dye molecules can form, which can cause changes in the structure of aggregates already present and the formation of more complex aggregates. In this work, we report the results of a study of the spectral properties of mixed three-component dye–polymer–fatty acid Langmuir–Blodgett films.

The structural formulas of the polyampholyte chain and dye **I** and **II** molecules are
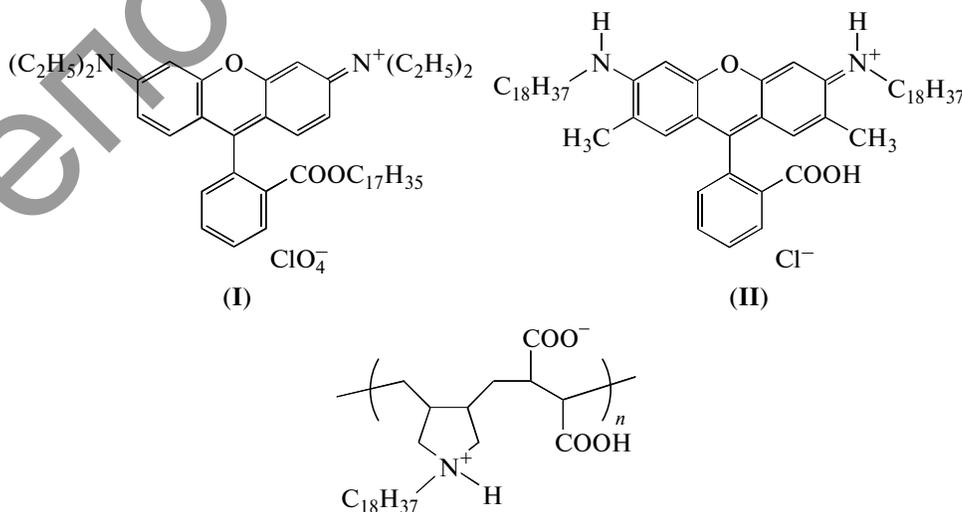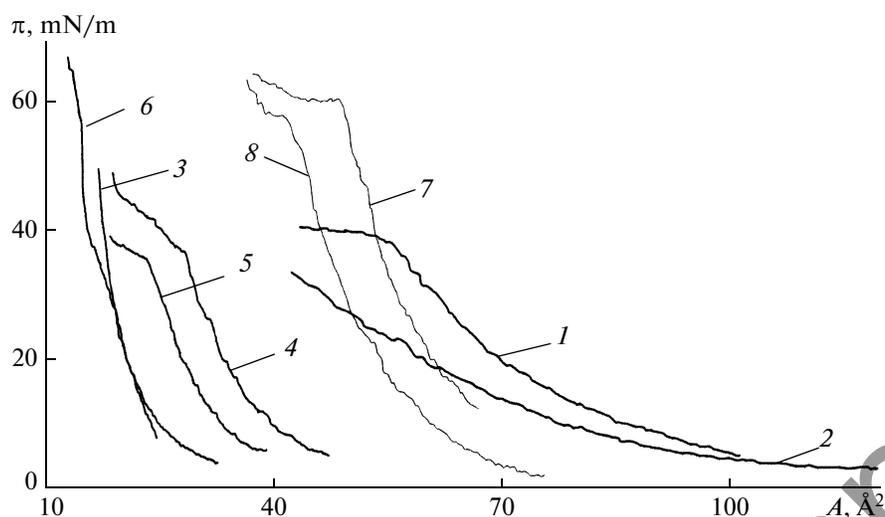
Fig. 1. Compression isotherms of mixed dye **I** monolayers: (*1*) polyampholyte; (*2*) dye; (*3*) stearic acid; (*4–6*) dye : stearic acid in ratios of 33 : 33, 22 : 44, and 11 : 55 (mol %), respectively; and (*7, 8*) dye : polymer in ratios of 50 : 50 and 17 : 83 (mol %), respectively.

The synthesis and characteristics of the amphiphilic polyampholyte were described in [4], and those of dyes, in [5].

EXPERIMENTAL

Monomolecular films were formed at the water/air interface in a Langmuir bath. We used doubly distilled deionized water. The surface tension of water was 72.8 mN/m at pH 5.6 and 17°C. Mixed monolayers were deposited on the aqueous subphase from a mixture of ethanol and chloroform taken in a 1 : 4 volume ratio. The concentration of the polymer in three-component monolayers was constant (33 mol %), and the ratio between the dyes and stearic acid (SA) was varied; it was 11 : 55, 22 : 44, and 33 : 33 (mol %). The isotherms of compression of monolayers were measured at 20°C. The transfer of monolayers onto substrates of nonluminescing quartz was performed by the vertical Z-type method at transfer pressures $\pi_{tr} = 30$ mN/m and the rate of plate movement through the monolayer 0.02 mm/s. The thickness of films was 20 monolayers.

RESULTS AND DISCUSSION

The compression isotherms of a pure polyampholyte layer at the water–air interface, dye **I**, stearic acid, mixed dye : SA monolayers, and dye : polymer monolayers are shown in Fig. 1. We see from Fig. 2 that three-component monolayers are in a more condensed state than two-component ones, which is evidence of a more compact arrangement of molecules. Similar data were obtained for dye **II**.

These results can be explained as follows. Polymer molecules are long chains, whose orientation on the surface of water is not linear; they can form loops with

various sizes. Packing of polymer chains is not compact, and the compression isotherm of a polymer monolayer corresponds to its liquid state. Dye molecules on the surface of the aqueous subphase can occupy voids formed by polymer chains. The monolayer then becomes more compact, which influences the compression isotherms of two-component dye monolayers. However, because of their size and spatial geometry, rhodamine dye **I** and **II** molecules do not fully occupy voids between polymer chains. The addition of stearic acid molecules to the two-component monolayer increases its density because fatty acid molecules have small cross section areas (~20 Å^2) [3] and fill the remaining voids in the monolayer.

Let us consider the results of spectroscopic studies of three-component Langmuir–Blodgett films. The absorption and fluorescence spectra of three-component Langmuir–Blodgett films of dyes **I** and **II** are shown in Figs. 2 and 3. The absorption spectrum of dye **I** contains two maxima. The more intense maximum corresponds to the monomeric band, and the short-wave maximum seen as a shoulder is evidence of the presence of sandwich-type dimers. The absorption spectrum of Langmuir–Blodgett films of dye **II** also consists of monomeric ($\lambda_{max} = 540$ nm) and dimeric ($\lambda_{max} = 508$ nm) bands.

The fluorescence spectrum of dye **I** contains two maxima, monomeric at $\lambda_{max} = 585$ nm and dimeric at $\lambda_{max} = 610$ nm; they are well defined compared with two-component films. As the content of stearic acid increases, the intensity of the monomeric Langmuir–Blodgett film band decreases, and the long-wave dimeric band becomes more intense. Characteristically, the fluorescence spectra of dye **II** in films with a large dye content contain three maxima. The middle and long-wave maxima correspond to the lumines-
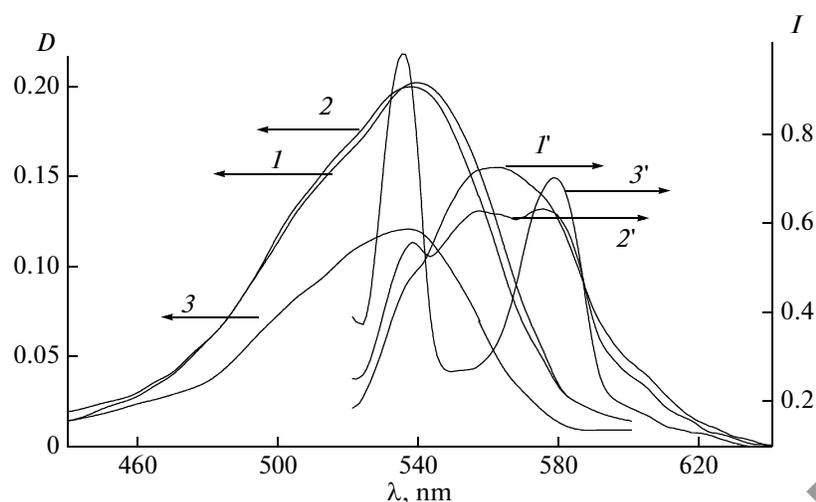
Fig. 2. (*1*–*3*) Absorption and (*1'*–*3'*) fluorescence spectra of three-component Langmuir–Blodgett films of dye **I** with SA and polyampholyte at dye : SA ratios of (*1*, *1'*) 33 : 33, (*2*, *2'*) 22 : 44, and (*3*, *3'*) 11 : 55 (mol %).
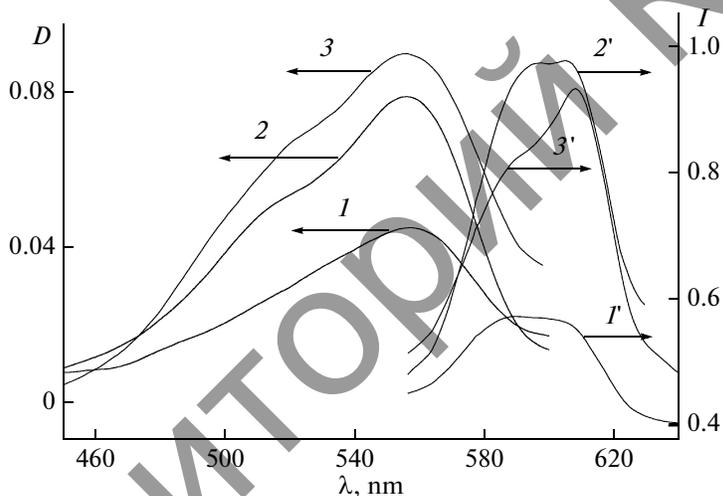

Fig. 3. (*1*–*3*) Absorption and (*1'*–*3'*) luminescence spectra of three-component Langmuir–Blodgett films of dye **II** with SA and polyampholyte at dye : SA ratios of (*1*, *1'*) 33 : 33, (*2*, *2'*) 22 : 44, and (*3*, *3'*) 11 : 55 (mol %).

cence of monomers and planar dimers, respectively, and the short-wave maximum corresponds to so-called H-aggregates formed of sandwich-type dimers [6]. The ratio between the numbers of monomers and aggregates depends on the concentrations of dye and stearic acid molecules. An increase in the fraction of stearic acid in Langmuir– Blodgett films results in an increase in the number of planar dimers and H-aggregates. The absorption band of planar dimers in the overall absorption spectrum is unnoticeable because of overlap with the intense absorption band of monomers.

Dye **I** and **II** molecules are known to form immiscible monolayers with stearic acid [7, 8]. The distribution of dye and stearic acid molecules in a monolayer can then be inhomogeneous and have the form of clus-

ters. As the number of stearic acid molecules increases, clusters of dye molecules as though become denser, and the probability of aggregation processes in them increases, which manifests itself in the absorption and fluorescence spectra of Langmuir–Blodgett films. Dye **II** molecules have two hydrophobic tails, and interaction between them additionally stabilizes the sandwich-type configuration of dimers. The number of such dimers increases in Langmuir– Blodgett films of dye **II**, and they form H-aggregates in three-component films.

The results of this study show that aggregates with various structures and films with various spectral and fluorescence properties can be formed by creating three-component Langmuir–Blodgett films of dyes **I**

and **II** and varying the concentrations of dye molecules, polymer, and stearic acid.

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