MACROMOLECULAR CHEMISTRY AND POLYMERIC MATERIALS

Polymeric Langmuir–Blodgett Films Containing Xanthene Dyes

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Abstract—Spectral and protolytic properties of two hydrophobic rhodamine dyes and fluorescein *n*-decyl ester were studied in Langmuir–Blodgett films based on a polyamido acid. The possibility of weakening the concentration quenching of rhodamine dye fluorescence with a polymeric matrix was demonstrated.

The Langmuir–Blodgett (LB) procedure allows preparation of nanosize highly ordered layers of biphilic molecules with exactly controllable thickness and directed orientation in space [1, 2]. Preparation of LB films (LBFs) containing dyes is of special interest because their optical and protolytic properties allow development various sensors in this way [3–8].

Xanthene dyes having high extinction coefficient and quantum yield of fluorescence are suitable for this purpose. Monolayers of rhodamines in stable matrices were studied in [3, 9–16]. Xanthenes are important group of dyes used in lasers [12], as photosensitizers [16], and in many other fields of photophysics and photochemistry. Both general questions of formation of mono- and *N*,*N*'-dioctadecylrhodamine B multilayers in various matrices (arachic acid and methyl arachate [9], dipalmitoylphosphatidic and dioleylphosphatidic acids [10]), and the ability of phosphors to form aggregates in films [10] have been considered. Preparation of *N*,*N*'dioctadecylrhodamine B monolayers on a subphase containing sodium lauryl sulfate was described in [11].

LBFs containing dyes in polymeric matrices have been studied to a considerably lesser extent. At the same time, films based on polymers are widely used owing to their high mechanical and chemical stability [1]. To obtain multilayer LBFs, polyamido acids (PAAs) are often used [1, 3, 4]. The structural formula of one of PAAs, poly(4,4'-diphenyl oxide)-2-carboxyisophthalamide (R = H) is shown below:
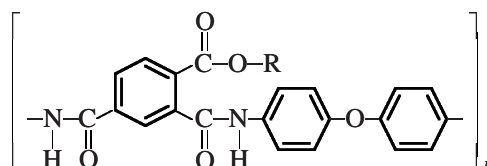
To make PAA macromolecules more hydrophobic, alkyl chains [R = $(CH_2)_{17}$–CH_3] are introduced into the PAA structure, or amines are added to form salts [17, 18]. To retain polymeric monolayers with carboxylic groups on the water surface, subphases containing metal ions are also used [1, 19, 20].

In this study, we prepared LBFs based on PAA containing immobilized xanthene dyes and examined properties of such well-ordered systems. Hydrophobic (lipoid) dyes: Rhodamine B *n*-heptadecyl ester perchlorate **1**: X^1 = *n*-$C_{17}H_{35}$, X^2 = X^3 = C_2H_5, Y^- = ClO_4^-, and *N*,*N*'-dioctadecylrhodamine chloride **2**: X^1 = X^2 = H, X^3 = *n*-$C_{18}H_{37}$, Y = Cl^-

1, 2
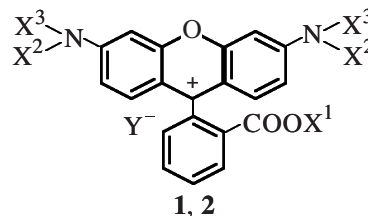
and fluorescein *n*-decyl ester **3**, whose structural formulas (for the molecular and ionic form) will be presented below, were chosen as investigation objects. To prepare monolayer films, the above dyes were added to matrices that can form stable layers on the water surface. It should be taken into account that xantenes can form dimers in various matrices [21], which leads to concentration quenching of the fluorescence and to worsening of the luminophore performance. These luminophores are also used as probes; in a number of cases, they allow estimation of local electrostatic potentials [22]. Therefore, the goal of this study was not only to develop methods for preparing polymeric xantene-containing LBFs, but also to determine the optimal conditions of their probable functioning as elements of sensor devices.

EXPERIMENTAL

Dyes were synthesized by methods described in [23, 24] and identified by elemental analysis, ^{1}H NMR, and TLC. Stearic acid, *n*-octadecyl alcohol (ODA), and *n*-octadecylpyridinium bromide (ODPB), and also surfactants used in experiments with aqueous micellar solutions [cetylpyridinium chloride (CPC), cetyltrimethylammonium bromide, cetyldimethylammoniopropanesulfonate, and sodium lauryl sulfate] were purchased from Fluka (as a rule, they contained 99% main substance). Buffer mixtures were prepared from chemicals of chemically pure grade. Oligomeric PAA with a molecular weight of the chain unit of 374 g mol^{-1} was used.[1]

The initial 1×10^{-3} M PAA solutions were prepared in a 1 : 1 mixture of chemically pure dimethylformamide and chloroform, and the initial solutions of stearic acid, ODA, and ODPB of the same concentration, in chloroform. Pb(NO$_3$)$_2$ was of chemically pure grade. Before an experiment, a bath was successively treated with 96% aqueous ethanol and chloroform and then filled with double-distilled water or a lead nitrate solution. Double-distilled water or a 1×10^{-5} M lead salt solution was used as a subphase; a decrease in the salt concentration makes weaker the influence of lead ions on the polymer.

Measurements were performed in a Langmuir bath with two 6.5×60 cm sections. The surface pressure π was recorded with a Wilhelmy balance (measurement error ± 0.3 mN m^{-1}) at $20 \pm 5°$C. An organic

solvent containing PAA was applied onto the water surface, and the system was allowed to stand for 5 min (time required for a monolayer to spread over the surface of the aqueous subphase, evaporation of the solvent, and accommodation of polymeric molecules). Then, the monolayer formed was compressed by an unwettable mobile barrier at a 3 cm min^{-1} velocity to a required pressure, which was then automatically kept constant.

The state of monolayers on the surface of the aqueous subphase was studied by plotting the π–A compression isotherms, where A is the surface area per recurring chain unit (Å^2). The limiting surface area S_m occupied by one chain unit was found by extrapolation of the linear portion of the isotherm to the abscissa; the determination error was $\pm(1$–$3)$ Å^2. From the compression isotherms, we determined the optimal surface pressure of applied monolayers corresponding to the most condensed state (in the middle of the linear portion). To prepare a mixed monolayer, the dye dissolved in chloroform was added to a mixture of PAA and *n*-octadecyl alcohol (or *n*-octadecylpyridinium bromide), or stearic acid, and then the resulting mixture was applied dropwise onto the surface of the aqueous subphase.

Monolayers were deposited onto glass or quartz plates by the Scheffer method; in so doing, π was 35 mN m^{-1} in the case of **1** and 30 (25) mN m^{-1} for **2** (in stearic acid or ODPB matrix, respectively). The pressure of transfer for the PAA + ODPB + **3** mixture was 25 mN m^{-1}. Prior to monolayer deposition, supports were pretreated with a peroxide–ammonia mixture and then washed with double-distilled water, acetone, and chloroform [3].

The glass supports with deposited multilayers of ODPB + **2** and PAA + ODPB + **3** were kept for 5 and 1 min, respectively, in aqueous solutions with known pH and dried for several minutes in air. It has been shown previously that introduction of a lead salt into the subphase is the optimal method for stabilization of PAA monolayers on the water surface [20]. Pb^{2+} ions can pass into the aqueous phase because of the interaction with Br$^-$ ions introduced with ODPB. However, special experiments showed that only a small part of lead ions pass into the aqueous phase. The Pb^{2+} content of the monolayers was monitored by analysis of LBFs by X-ray photoelectron spectroscopy (Kratos XPS-800 spectrometer; photoelectrons were excited by Al(Mg)$_{K_\alpha}$ radiation; power of X-ray tube 15 kV $\times$ 20 mA).

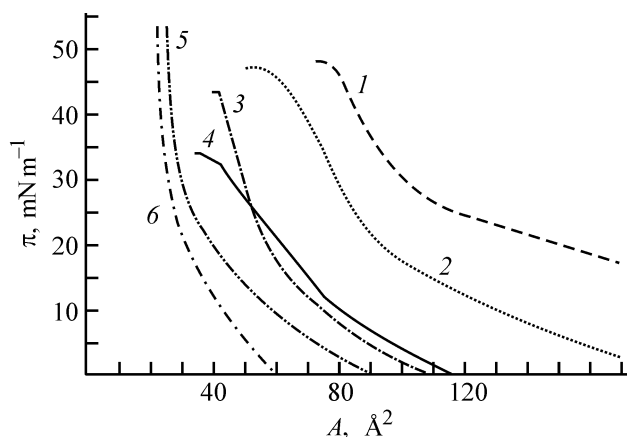The pH value [$\pm(0.01$–$0.04)$] was monitored with a glass electrode in an electric circuit with transfer.

Fig. 1. Surface pressure π vs. the surface area A per repeating unit of polymer for different systems: (*1*) PAA : ODPB = 1 : 1 + 28 mol % **1**, (*2*) PAA : ODA = 1 : 1 + 22 mol % **1**; (*3*) PAA : ODA = 1 : 1, (*4*) PAA : ODPB = 1 : 1, (*5*) stearic acid + 3 mol % **1**, and (*6*) stearic acid + 1.5 mol % **1**. Dependences (*1–4*) were obtained with films prepared on a Pb^{2+}-containing subphase. The dye concentration is expressed in molar percent relative to the total number of moles of the components in the mixture.
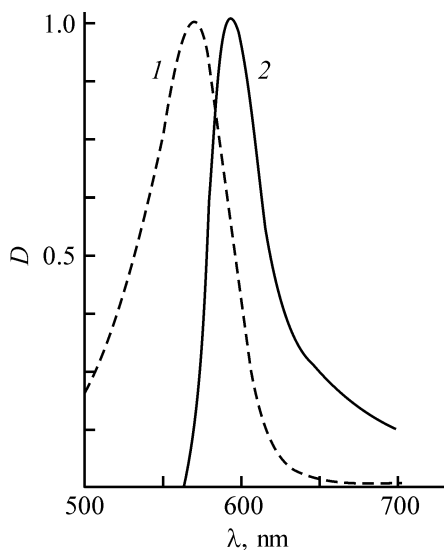

Fig. 2. (*1*) Absorption and (*2*) fluorescence spectra of dye **1** in PAA : ODPB = 1 : 1 + 6 mol % **1** film. Film was applied by the scheme ABBBABBB ($n = 60$, $N = 240$). (*D*) Optical density and (λ) wavelength; the same for Figs. 3–5.

The absorption spectra of films containing dyes were recorded on a Specord M 40 spectrophotometer, and the fluorescence spectra, on a Hitachi F-4010 spectrophotometer; the films without dyes were used as reference samples.

The fluorescence of LBFs containing dyes **1**–**3** was extremely weak. This may be due both to probable aggregation (dimerization) of dye molecules and to concentration quenching. Therefore, we recorded fluorescence using the method described in [10]. A multilayer structure was prepared by alternation of layers ABBBABBB (A is a layer of a dye-containing mixture, prepared on a Pb^{2+}-containing subphase; B is ODPB layer prepared on a pure subphase). Such a separation of layers containing a dye (their number *n* in all cases was 60) leads to a sharp enhancement of the fluorescence, despite that the pyridinium ring also exerts a quenching effect. The total number of layers we denoted as *N*.

Preliminarily, we studied the behavior of monolayers of PAA + ODA and PAA + ODPB mixtures on the surface of both pure and lead-containing water subphases. The surface areas per repeating unit of the polymer for the mixtures PAA : ODA = 1 : 1 (counting on repeating unit, $S_m = 62$ Å^2) and PAA : ODPB = 1 : 1 ($S_m = 92$ Å^2), evaluated from the compression isotherms, agree with the values published earlier for similar systems [18].

Typical compression curves for mixed layers containing dye **1** are shown in Fig. 1. Introduction of a dye into the matrix of stearic acid increases the surface area per molecule from 27.5 [content of dye **1** 1.5 mol %] to 33.4 Å^2 (3 mol %). At a dye content of 22 mol % in the PAA : ODA = 1 : 1 mixture, the maximal surface area increases to 112.7 Å^2 (in the mixture without dye, it is about 56 Å^2). The S_m value in the PAA : ODPB = 1 : 1 mixture increases from 92 to 131 Å^2 upon introduction of 28 mol % hydrophobic rhodamine **1** into the film. Figure 1 shows that mixtures without dye form a denser monolayer whose loosening becomes possible when large dye molecules are introduced.

The absorption and fluorescence spectra (wavelength of fluorescence excitation $\lambda = 520$ nm) of polymeric films containing dye **1** are shown in Fig. 2. The absorption and fluorescence peaks (±2 nm) are observed at 564 and 593 nm, respectively. For aqueous micellar solutions of both cetyltrimethylammonium bromide and sodium lauryl sulfate at a surfactant concentration of 0.01 M, these values are 555 and 579 nm, respectively, and binding of dye molecules insoluble in water with surfactant micelles is beyond any doubt. The red shift of both bands in the LBF spectra, compared to the spectra of aqueous micellar solutions, suggests a more dehydrated surrounding of the dye molecules in the multilayers.

With increasing content of dye **1** in LBF of both stearic acid and PAA + ODPB, the absorption maximum is shifted bathochromically from 564 to

Table 1. Effect of matrix on the D_2/D_1 ratio in multilayer films ($n = N = 60$) containing (**1**) Rhodamine B n-heptadecyl ester and (**2**) N,N'-dioctadecylrhodamine

System	Dye concentration, mol %	Method of film preparation	Absorption, λ_{max}, nm (± 2)	D_1/D_2 ratio
LBF:				
PAA + ODPB + **1**	28	LB	570	0.50 ± 0.06
PAA + ODA + **1**	17.3	LB	568	0.55 ± 0.03
Stearic acid + **1**	6.5	LB	570	0.65 ± 0.03
Stearic acid + **1**	6.5	Casting	570	0.71 ± 0.03
1	100	"	572	0.80 ± 0.05
PAA + ODPB + **1**[*]	6	LB	570	0.42 ± 0.02
PAA + ODA + **1**[*]	6	LB	570	0.44 ± 0.02
Aqueous micellar solutions + **1**	10^{-5}–10^{-6} M	–	555	0.25
LBF:				
PAA + ODPB + **2**[**]	2	LB	543	0.77 ± 0.02
ODPB + **2**	2	LB	543	0.75 ± 0.05
Aqueous micellar solutions + **2**	10^{-5}–10^{-6} M	–	525–530	0.28 ± 0.33[***]

[*] Films were prepared with the introduction of sandwiching layers of ODA ($n = 60$, $N = 240$). The other films were prepared without additional ODA layers ($n = 60$).

[**] The data are related to the zwitterionic form of dye **2**, prevailing in neutral and alkaline media.

[***] For cationic form of dye **2** (measurements at HCl concentration of 0.06 M), 0.29–038.

572 nm. In going from the polymeric matrix to stearic acid and neat dye film prepared by casting, the intensity of absorption in the region of 530 nm increases and the absorption band becomes strongly broadened (Table 1, Fig. 3), which may be caused by formation of dimers and other aggregates of the dye upon an increase in its content in the film.

The main spectral maximum of monomer **1** in the LBF spectrum lies at $\lambda_1 \sim 570$ nm. The short-wave shoulder caused by the vibrational structure of the spectrum lies at $\lambda_2 \sim 530$ nm, as in the spectra of sandwich-type dimers [10]. The presence of dimers in the film studied (Fig. 3) is usually judged from the ratio of the absorption intensities at λ_2 and λ_1 (D_2/D_1). For systems with monomers, this ratio falls within 0.3–0.5 [10, 15]. Ishibashi et al. [14] reported a decrease in D_2/D_1 when the matrix with the maximal surface area at the phase boundary (dipalmitoylphosphatidylcholine as compared to dipalmitoylphosphatidic acid) was used. The decrease in D_2/D_1 was also noted [10] when dioleylphosphatidic acid characterized by a larger surface area of the molecule as compared to dipalmitoylphosphatidic acid was used.

The D_2/D_1 ratio for dye **1** is greater in stearic acid in comparison with the polymeric matrix and is considerably greater in the neat dye film prepared by casting (Table 1, Fig. 3). It is interesting that the use of both ODPB and ODA for PAA stabilization at the wa-

ter–air interface shows the same effect of a decrease in the number of dimers in monolayers containing dye **1**. This can be accounted for by the fact that the polymer chain stabilized by a long-chain alcohol or amine molecule occupies larger surface area on the surface of the water subphase as compared to stearic acid molecule. As a result, in the polymeric multi-
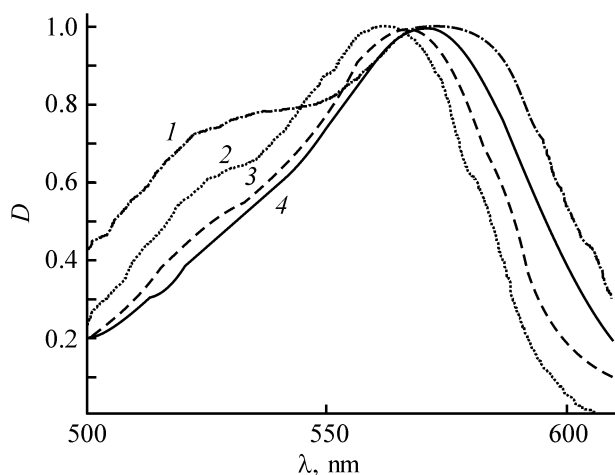

Fig. 3. Normalized absorption spectra of dye **1** in films. Film: (*1*) applied by casting of neat dye **1**; (*2*) stearic acid + 6.5 mol % **1**; (*3*) mixed PAA : ODPB = 1 : 1 + 17.3 mol % **1**; and (*4*) mixed PAA : ODPB = 1 : 1 + 28 mol % **1**. Films (*2–4*) are prepared on a Pb^{2+}-containing subphase ($n = N = 60$).

Table 2. Spectral properties of N,N'-dioctadecylrhodamine **2** in LBFs of various compositions

System[*]	pH of solution for support treatment	Sandwiching layers	Transfer pressure, mN m^{-1}	λ_{max}, nm (± 1)	
				absorption	fluorescence
PAA : ODPB = 1 : 1	6	No	30	543	590
	1.2	Yes	30	551	592
	6	"	30	543	573
	6	No	15	543	583
ODPB	6	"	25	542	–
	1.5	"	25	550–551	–

[*] PAA : ODPB ratio per repeating unit; the mole fraction of dye **2** is equal to 2%.

layers, the volume concentration of dye molecules becomes smaller, and they become more isolated from each other at virtually the same molar concentration in the monolayer (Fig. 3).

Introduction of intermediate ODA layers into the PAA + ODPB + **2** (2 mol % dye) film does not substantially change the D_2/D_1 ratio (0.79). At the same time, in 50 and 88 wt % aqueous ethanol, in 0.005 M solutions of cetyltrimethylammonium bromide and sodium lauryl sulfate, and in 0.001 M solution of sodium cetyldimethylammoniopropanesulfonate, the D_2/D_1 ratio for the acid and alkaline dye forms vary within 0.288–0.380 and 0.275–0.332,

Fig. 4. (*1*) Absorption and (*2*) fluorescence spectra of PAA : ODPB = 1 : 1 + 2 mol % dye **2** films. Film was applied by the scheme ABBBABBB ($n = 60$, $N = 240$) at $\pi = 30$ mN m^{-1}; (*3*) fluorescence spectrum of the same film after treatment with a solution with pH 1.3 for 3 min; (*4*) absorption spectrum of ODPB + 2 mol % **2** ($n = N = 60$) film.

respectively. Since the dye concentration was 2×10^{-6} M, the monomer is the dominant form here.

To obtain monolayers containing dye **2**, we used matrixes able to form monolayers at the water–air interface, because by applying neat dye **2** onto the surface of the water subphase ($\sim 10^{-5}$–10^{-7} M) we failed to obtain a film with a sufficient surface pressure. This observation is in accordance with data for the other dyes [9].

Applying layers of ABBBABBB type causes a shift to shorter wavelengths (574 nm) as compared to alternate application of the monolayers (583 and 590 nm at a transfer pressure of 15 and 30 mN m^{-1}, respectively). Such effects are described in [10] and are associated with the dye concentration in the monolayer with increasing 2D compression.

Dye **2** containing a free carboxy group can change its spectral properties with the acidity of the medium (Table 2, Fig. 4). The absorption and fluorescence peaks in the spectra of the initially prepared film lie at 543 ± 1 and 583 ± 1 nm, respectively, but after its immersion into an acid medium (aqueous HCl solution with pH 1.3) both bands are red-shifted. Similar features are observed upon introduction of dye **2** into an ODPB film. The band shift is associated with the transition of the dye molecule into the protonated form. At the same time, in micellar solutions of various surfactants, the above values of λ_{max} are lower by 20–30 nm than those for LBF, which, as in the case of dye **1**, suggests the more dehydrated surrounding of rhodamine **2** as compared to aqueous micellar solutions.

Fluorescein n-decyl ester **3** is one of dyes with a pH response, used for study of lyophilic dispersions [22, 26]. The possibility of preparing a Langmuir monolayer of neat dye 3 and its mixture with stearic acid was examined in [16]. In this study, we prepared
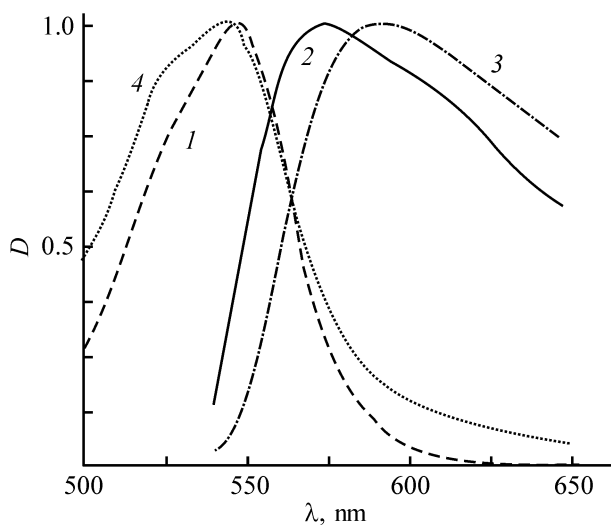
Table 3. Parameters of equilibrium for fluorescein *n*-decyl ester **3** in various systems

Parameter	LBF PAA : ODPB = 1 : 1	Aqueous solution of CPC with addition of 0.4 M NaCl	Aqueous solution of fluorescein ethyl ester as homolog of **3** [22]
λ_{max}, H_2R^+, nm	456	449	438
λ_{max}, HR, nm	470, 505	465, 490	450, 465
λ_{max}, R^-, nm	525	516	491
pK_{a0}^a	1.63 ± 0.10	1.32 ± 0.01	2.94
pK_{a1}^a	6.48 ± 0.16	5.52 ± 0.02	6.31

colored and fluorescent multilayer polymeric films based on this dye. Depending on pH of the solution, three forms of **3** exist: cationic (H_2R^+), molecular (HR), and anionic (R^-) [22, 26]:
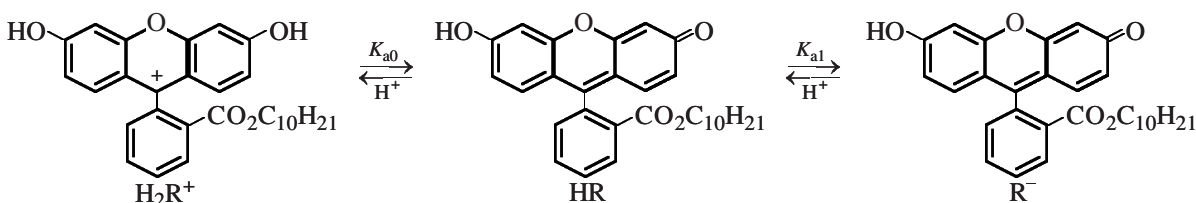
After treatment of the support with acid solutions, dye **3** in multilayers transforms into the H_2R^+ form, which is undoubtedly confirmed by the existence of a strong absorption band at 456 nm (Fig. 5). At high pH, dye **3** in LBF transforms into anion R^- (Fig. 5, band at 525 nm). After treatment with solution with pH 2.6 (Fig. 5), a three-band spectrum characteristic of the molecular form HR is observed [22, 26]. Thus, in LBF, two steps of protolytic transformations of dye **3**, $H_2R^+ \rightleftarrows HR + H^+$ and $HR \rightleftarrows R + H^+$, are also observed. In the course of experiments, LBF was immersed into aqueous solutions whose pH was adjusted with acetate, phosphate, and borate buffer solutions and with HCl; as a rule, the ionic strength of the solution was kept constant (0.05 M) by NaCl additions.

The spectra of micellar solutions are, on the whole, similar, but all values of λ_{max} are noticeably lower (Table 3). This fact confirms the conclusion made above for rhodamines **1** and **2** about dehydration of LBF dried in air. The apparent ionization constants pK_{a0}^a and pK_{a1}^a for dye **3** in LBF and micellar CPC solution and the same parameters for a short-chain analog, fluorescein ethyl ester, found by the standard spectrophotometric method [26] are listed in Table 3.

Both values of pK_a^a for CPC in micellar solutions are lower than those in aqueous solutions, which is associated with the positive charge of the micellar surface, at which ionized groups are probably localized

[22, 26]; at lower concentration of the supporting electrolyte (0.05 M instead of 0.4 M NaCl), the pK_a^a values are still lower: pK_{a0}^a 0.79 ± 0.10 and pK_{a1}^a 4.92 ± 0.07 [22]. In the case of LBF of composition PAA + ODPB at low pH values, the dye surrounding
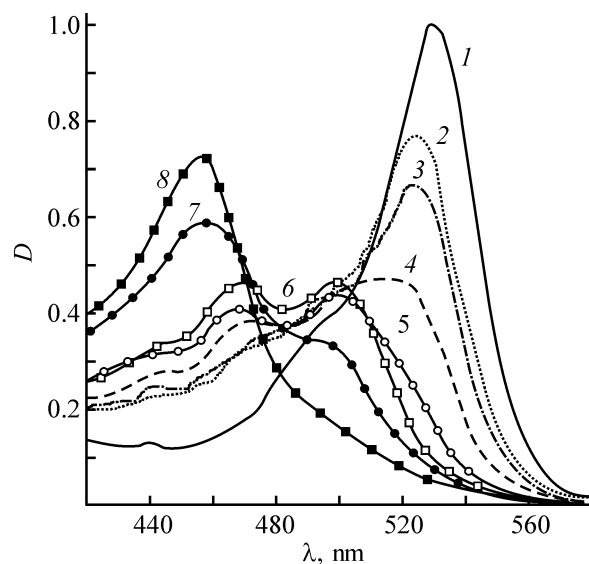

Fig. 5. Absorption spectra of fluorescein *n*-decyl ester in the PAA : ODPB = 1 : 1 ($n = N = 60$) film after its treatment for 1 min in aqueous solutions with pH (*1*) 11.2, (*2*) 8.6, (*3*) 7.0, (*4*) 6.1, (*5*) 4.26, (*6*) 2.6, (*7*) 1.4, and (*8*) ≤1.1. Films were obtained on a Pb^{2+}-containing subphase at pH 5.8; dye **3** content 13 mol %.
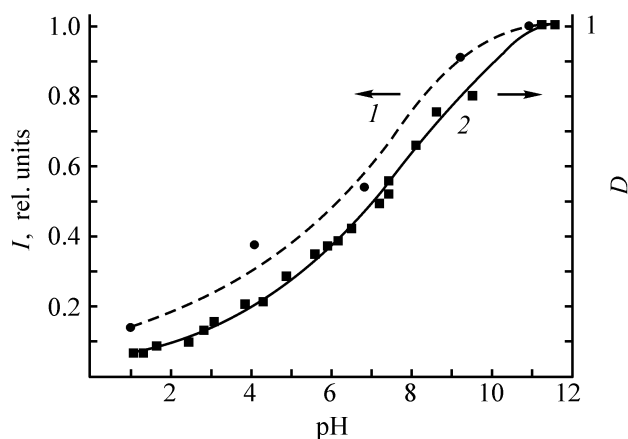
Fig. 6. pH dependence of the intensity *I* of (*1*) fluorescence and (*2*) absorption of LB film (PAA : ODPB = 1 : 1). Mole fraction of dye **3** in the film 13%; time of film immersion in aqueous buffer solution 1 min at 20°C; optical density was measured at 525 nm, and fluorescence, at 552 nm; Wavelength of fluorescence excitation 500 nm. Luminescence was measured for a film with $n = 60$ and $N = 240$, and absorption, for a film with $n = N = 60$.

is close to that in CPC micelles, whereas with increasing pH the carboxy groups in the polymer undergo ionization, the charges of the carboxylate and pyridinium ions are mutually neutralized, and the pK_{a1}^{a} value corresponds to a weakly charged or even neutral layer.

From the viewpoint of the practical use of such LBFs, it is important how the optical density and fluorescence intensity respond to changes in the pH of the aqueous phase in which the films are immersed. In the case of dye **3**, the transition interval covers the physiological range of pH values (Fig. 6). Unusual for acid-base indicators extension of the transition interval is of interest. Such "nonclassical" phenomena are typical of complex sensor devices [27, 28]. They may be associated with the multiplicity of localization sites of the dye in the film and with the existence of islets of the neat dye. In CPC micellar solutions (Table 3) and in other colloidal systems [22, 26], the transition intervals are quite traditional.

In general, unambiguous interpretation of the indicator behavior in sensors is a complex problem [29]. A series of fluorescent pH sensors based on derivatives of fluorescein *n*-octadecyl ester (without using LBF) was examined by Wolfbeis et al. [30, 31].

The measurements performed showed that the pH dependences of the absorption and fluorescence (Fig. 6) are well reproducible and can be used as calibrating curves in optical sensors. The films studied do not decompose and do not change their properties for two years, if kept in the dark at room temperature.

The growth of the fluorescence intensity in the physiological region of pH allows use of multilayer polymeric films based on compound **3** as elements of sensor devices in biochemical studies.

CONCLUSIONS

(1) Langmuir–Blodgett multilayer films containing xanthene dyes Rhodamine B *n*-heptadecyl ester, *N,N'*-dioctadecylrhodamine, and fluorescein *n*-decyl ester were prepared on the basis of a polyamido acid. Their spectral-luminescence and acid–base properties were studied.

(2) The use of a polymeric matrix makes lower the possibility of formation of dimers from Rhodamine B *n*-heptadecyl ester and *N,N'*-dioctadecylrhodamine in Langmuir–Blodgett films.

(3) Changes in the light absorption and fluorescence of the indicator, fluorescein *n*-decyl ester, immobilized in a polymer matrix, observed in the physiological range of acidities, are well reproducible and can be used to prepare stable ultrathin nanodimensional pH-sensitive sensor films for multiple use.

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