

Langmuir-Blodgett films of binary mixtures for polymethylmethacrylate/rubrene and stearic acid/rubrene: formation conditions and optical properties

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Received June 26, 2006

Polymorphism of polymethylmethacrylate/rubrene and a stearic acid/rubrene monolayers depending on concentration of luminophore immobilized in the film has been studied. The maximum rubrene concentration has been determined at which phase separation in monolayers of the binary systems is not observed. It is revealed that in multilayer Langmuir-Blodgett films with immobilized rubrene molecules, its content is higher in the polymer film than in stearic acid. The rubrene concentration in Langmuir-Blodgett films of polymethylmethacrylate grows linearly with increasing carry pressure. It is found that at exposure of films in bidistilled water at 22°C for 45 min, the luminophore content in the films decreases by at most 40 %.

Исследован полиморфизм монослоев полиметилметакрилат/рубрен и стеариновая кислота/рубрен в зависимости от концентрации иммобилизованного в пленке люминофора. Определена максимальная концентрация рубрена, при которой не наблюдается фазовое разделение в монослоях бинарных систем. Обнаружено, что в мультислойных пленках Ленгмюра-Блоджетт с иммобилизованными молекулами рубрена его содержание больше в полимерной пленке, чем в стеариновой кислоте. Концентрация рубрена в пленке Ленгмюра-Блоджетт полиметилметакрилата растет линейно с увеличением давления переноса. Установлено, что при экспонировании пленок в бидистиллированной воде при температуре 22°C в течение 45 минут содержание люминофора в пленках уменьшается максимум на 40 %.

The Langmuir-Blodgett (LB) method, allowing to obtain molecular mono- and multilayers of low and high molecular organic compounds with controllable thickness and molecular orientation, is now used widely in various areas of science and engineering, particularly in biosensor development, non-linear optics, nanoelectronics, etc. [1–3].

Most luminophors of good prospects, including rubrene, cannot form independently monomolecular LB layers at the water/air interface. In such cases, mixed solutions are used to provide stable monomolecular layers of hydrophobic compounds, where one com-

ponent is able to form the LB monomolecular layers [4, 5]. The well-known amphiphilic compounds such as fatty acids (stearic and arachidonic) and polymethylmethacrylate are often used as matrices for LB films [5, 6]. However, physical and chemical features of LB monomolecular layers formation in binary mixtures of lengmuirogenic and non-amphiphilic compounds on an aqueous subphase surface, the problem of multilayer LB film preparation, stability and luminescent properties remain poorly investigated to date. The purpose of this work is to study the formation features

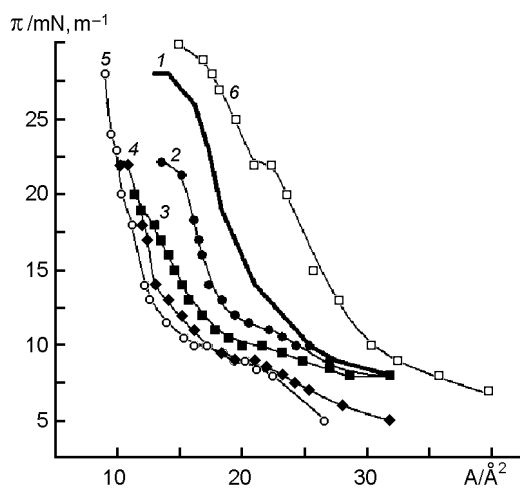


Fig. 1. π - A isotherms for (PMMA + rubrene) mixtures at rubrene content: 0 % (1); 10 % (2); 20 % (3); 30 % (4); 50 % (5); 100 % (6).

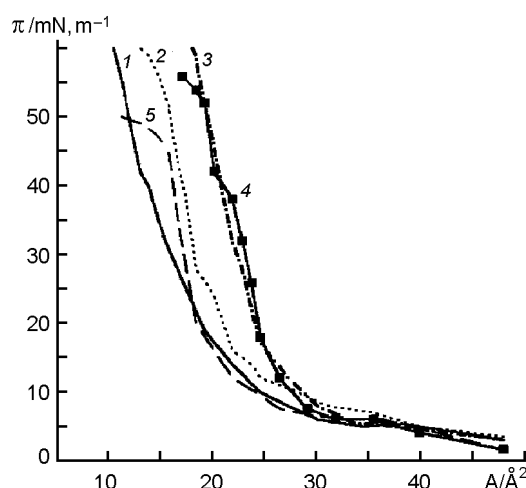
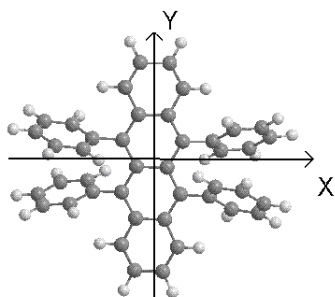


Fig. 2. π - A isotherms for (HSt + rubrene) mixtures at rubrene content: 0 % (1); 10 % (2); 20 % (3); 30 % (4); 50 % (5).

of Langmuir-Blodgett monomolecular layers in the of stearic acid/rubrene and polymethylmethacrylate/rubrene systems, the multilayer LB film formation processes and the spectral and luminescence properties thereof.

Polymethylmethacrylate (PMMA, molecular mass 100,000), stearic acid (HSt), and rubrene were used. The computer model of the rubrene molecule executed using the design technique AM1 (MOPAC) is presented below:



Initial solutions of $1 \cdot 10^{-3} \text{ M} \cdot \text{l}^{-1}$ concentration in chloroform of chemical purity

grade were prepared. The bidistilled water was used to prepare subphase. Formation of Langmuir-Blodgett monomolecular layers and of surface pressure/area per a molecule isotherms (π - A isotherms) were studied using equipment made at NIOPIK (Moscow). The surface pressure, π , was recorded using a Wilhelmy balance (to within $\pm 0.3 \text{ mN} \cdot \text{m}^{-1}$) at $20.0 \pm 0.5^\circ \text{C}$. The area per one structure unit in the monomolecular layer (A) was measured by extrapolating the rectilinear part of the isotherm to the X axis at an accuracy of $\pm (1-3) \text{ \AA}^2$. The pressure, at which the multilayered film structure was formed on the glass substrates by Schaefer method, was determined from the compression isotherms. The subphase pH value (6.00 ± 0.04) was monitored by an I-160M ionometer. The absorption spectra of LB films were measured by a Specord M 40 spectrophotometer, and luminescence spectra were measured using a SDL-2 device. The LB film composition was analyzed by X-ray photoelectron spectroscopy using a Kratos XPS-800 spectrometer.

Table 1. The characteristics of monomolecular layers of binary mixes PMMA/rubrene with the various contents of rubrene

$C_{rub}, \%$ mol. %	Compressibility, $\delta, \text{ m} \cdot \text{mN}^{-1}$			$A_{12}, \text{ \AA}^2$	$\pi_c, \text{ mN} \cdot \text{m}^{-1}$	$A_{rub}, \text{ \AA}^2$
	$\pi = 7, \text{ mN} \cdot \text{m}^{-1}$	$\pi = 12, \text{ mN} \cdot \text{m}^{-1}$	$\pi = 18, \text{ mN} \cdot \text{m}^{-1}$			
0	0.140	0.014	0.031	18.50	26	–
10	–	0.059	0.021	21.15	20	45
20	0.400	0.021	0.034	22.00	20	36
30	0.063	0.048	0.039	18.47	22	18.4
50	0.053	0.035	0.054	16.75	29	15

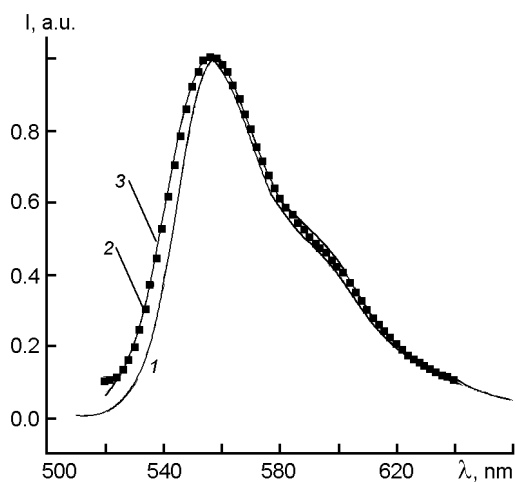


Fig. 3. Luminescence spectra of rubrene in a 36-monolayer films in different matrices: Rub/Chloroform — 1 (rubrene solution in chloroform, $1 \cdot 10^{-4}$ M/l $^{-1}$), PMMA — 2, HSt — 3 at rubrene content 20%. Spectra are normalized to maximum, $\lambda_{exc.} = 495$ nm.

Consideration of π -A isotherms presented at Figs. 1 and 2 shows (Tables 1 and 2) that parameters of the LB monomolecular layer in PMMA/rubrene and HSt/rubrene binary mixtures depend on the rubrene concentration and the surface pressure. The area per rubrene molecule was calculated according to a rule of additivity for noninteracting binary mixes [6, 7]:

$$A_{12} = N_1 A_1 + N_2 A_2, \quad (1)$$

where N_1 and N_2 are mole fractions; A_1 and A_2 area the areas per molecule of the first and second component, respectively; A_{12} area the average area obtained from compression isotherms. The areas of rubrene molecule projections (calculated for the model structure presented above) on the planes parallel to water/air interface and perpendicular to X-axis are about 125 \AA^2

and about 64 \AA^2 , respectively. The value obtained from the compression isotherms at 20 % rubrene content in the polymer matrix is 36 \AA^2 (Table 1). It is possible to suggest that such area corresponds to the molecular orientation at which benzene rings are inside of monomolecular layer and other part of rubrene molecule is pushed out to the surface of the monomolecular layer due to strong hydrophobic properties.

After introduction of luminophore into stearic acid monomolecular layer at an amount less than 20 mol.% (Table 2), the area of rubrene molecule projection on the subphase surface becomes about 76 \AA^2 . Thus, the rubrene positions in LB films of PMMA and HSt can be assumed to be different. In the PMMA/rubrene system, the rubrene molecule is partially displaced to the monomolecular layer while in the HSt/rubrene one, the luminophore molecule basic plane is positioned between alkyl chains.

The decreasing area per luminophore molecule observed at its rising concentration in considered LB films (Tables 1 and 2) can be caused by aggregation of rubrene molecules with their further release into a separate phase. This is especially appreciable when rubrene is introduced into film at the amount of 50 % and above (islands of luminophore phase on the aqueous subphase surface are visually observed).

For all studied rubrene concentration in PMMA matrix, a "plateau" is observed in the compression isotherms caused by change of luminophore molecules conformation in the matrix monomolecular layer. The collapse pressure in the LB films of HSt/rubrene system is higher considerably than in PMMA/rubrene LB films (Fig. 2, Table 2). Compressibility of monomolecular layers drops with pressure increasing, and in the intervals $\pi = 12$ to $19 \text{ mN} \cdot \text{m}^{-1}$ (PMMA/rubrene) and $\pi = 25$ to 50 mN/m (HSt/rubrene)

Table 2. The characteristics of monomolecular layers of binary mixes HSt/rubrene with the various contents of rubrene

$C_{rub, \%}$	Compressibility, δ , $\text{m} \cdot \text{mN}^{-1}$			A_{12} , \AA^2	π_c , $\text{mN} \cdot \text{m}^{-1}$	A_{rub} , \AA^2
	$\pi = 5$, $\text{mN} \cdot \text{m}^{-1}$	$\pi = 15$, $\text{mN} \cdot \text{m}^{-1}$	$\pi = 30$, $\text{mN} \cdot \text{m}^{-1}$			
10	0.074	0.019	0.013	21.5	58	66
20	0.039	0.024	0.006	32	58	76
30	0.173	0.017	0.011	31.5	55	56
50	0.059	0.005	0.005	24	46	27
0	0.072	0.019	0.044	20.5	58	—

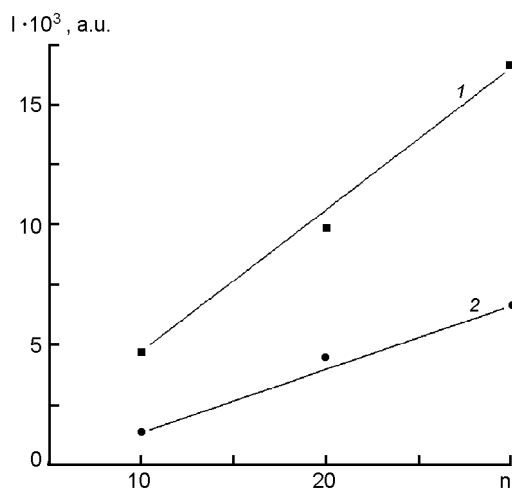


Fig. 4. The dependences of rubrene emission in Langmuir-Blodgett films PMMA/rubrene (1) on the n (number layers) at $\pi = 18 \text{ mN}\cdot\text{m}^{-1}$ and HSt/rubrene (2) at $\pi = 30 \text{ mN}\cdot\text{m}^{-1}$; rubrene 20 %.

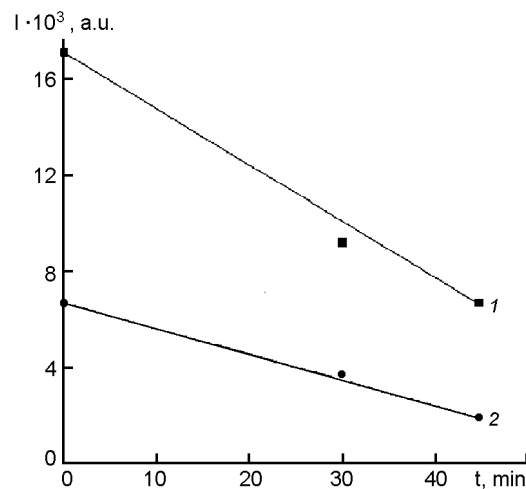


Fig. 5. Luminescence properties stability of PMMA/rubrene systems (1) and HSt/rubrene (2) vs substrate treatment time (PMMA/rubrene: $\pi = 18 \text{ mN/m}$; HSt/rubrene: $\pi = 30 \text{ mN/m}$); rubrene 20 mol.%, $n = 30$.

brene), the LB film becomes a liquid-crystal ($\delta = 10^{-2}$ to $10^{-3} \text{ m}\cdot\text{mN}^{-1}$ in the liquid crystal state [7]). The considered LB films are stable on the water surface, and are well transferable onto the glass substrates (the transfer coefficient of the monomolecular layer is close to 1).

The rubrene luminescence spectra in various matrices and in the chloroform solution are presented in Fig. 3. The rubrene luminescence intensity maximum in chloroform is at $\lambda_{max} = 559 \pm 1 \text{ nm}$, while in the LB films, at about $555 \pm 1 \text{ nm}$. The small hypsochromic shift is caused obviously by weak rubrene interaction with PMMA or HSt.

The linear luminescence intensity dependence on the number of layers suggests that each subsequent layer is transferred similarly to previous one (Fig. 4). With increasing superficial pressure at which the monomolecular layer is transferred onto the substrate, the luminescence signal increases linearly, too. Hence, the rubrene concentration in PMMA LB films increases linearly. A higher luminescence signal intensity in polymer LB film as compared to the stearic acid/rubrene LB film (by a factor of about 2.5) shows that in the first case, the number of rubrene molecules is greater. The relative change of the luminescence intensity in considered systems (when processing substrates in bidistilled water for 45 min) in stearic acid LB films is 0.65, and in polymer ones, 0.59 (Fig. 5). Thus, the stability of luminescent properties for LB

films in water solutions in PMMA/rubrene system is greater than in HSt/rubrene.

The XPS research of multilayer PMMA/rubrene LB films (20 mol.% of rubrene) has shown that even when 2 layers only are deposited, a continuous film of thickness not exceeding 10 nm is formed. After deposition of 6 layers, the signal from substrate is essentially absent (less than 1 %), that evidences the absence of pores in LB films.

To conclude, the polymorphism of PMMA/rubrene and HSt/rubrene monomolecular layers depending on the luminophore concentration immobilized in a film has been studied. The maximum rubrene concentration at which the phase separation in monomolecular layers of PMMA/rubrene and HSt/rubrene binary mixtures is not observed has been determined. Influence of a matrix on rubrene orientation in the formed LB film has been revealed. In stearic acid matrix, the luminophore molecules are oriented with the basic plane between molecules of surfactant while in PMMA matrix, they are partially displaced above the monomolecular layer. The rubrene maximum luminescence in LB films is shifted hypsochromically with respect to that in its chloroform solution, that is caused by weak luminophore interaction of with PMMA or HSt. It has been shown that at formation of the multilayer films containing rubrene molecules in PMMA and HSt matrixes, each subsequent layer is carried as the previous one. The transfer coefficient is close to

unity. At the same number of monomolecular layers in multilayer LB films, the luminescence intensity, and so the rubrene concentration, is higher in PMMA matrix than in HSt one. The rubrene concentration in LB PMMA film grows linearly with increase of transfer pressure. The luminescence intensity of LB films on glass substrates has been established to decrease approximately equally for both systems at films exposure in bidistilled water at 22°C.

This work is supported in part by STCU grant #G-77.

Acknowledgments. Authors are thankful to Dr.O.A.Zhikol for the help in calculations and participation in discussion of results.

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Дослідження умов формування та оптичних властивостей плівок Ленгмюра-Блоджетт бінарних систем поліметилметакрилат/рубрен та стеаринова кислота/рубрен

О.Н.Безкровна, Ю.М.Саввін, М.В.Добротворська

Досліджено поліморфізм моношарів поліметилметакрилат/рубрен і стеаринова кислота/рубрен залежно від концентрації іммобілізованого у плівці люмінофора. Визначено максимальну концентрацію рубрену, при якій не спостерігається фазовий розподіл у моношарах бінарних систем. Виявлено, що у мультишарових плівках Ленгмюра-Блоджетт із іммобілізованими молекулами рубрену його вміст буде більшим у полімерній плівці, ніж у плівці поверхнево-активної речовини. Концентрація рубрену у Ленгмюра-Блоджетт плівці поліметилметакрилату зростає лінійно зі збільшенням тиску переносу. Встановлено, що при експонуванні плівок у бідистильованій воді при температурі 22°C на протязі 45 хвилин вміст люмінофора у плівках зменшується не більш, ніж на 40 %.