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Stilbazolium merocyanine systems in Langmuir and Langmuir–Blodgett molecular layers

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ABSTRACT

Stilbazolium merocyanine (1-(12-hydroxydodecyl)-4-[(3-hydroxy-4-oxocyclohexa-2,5-dienylidene)-ethylidene]-1,4-dihydropyridine) was investigated in form of Langmuir and Langmuir–Blodgett films for potential sensor of environment pH and presence of metal ions applications. Two forms of the merocyanine, free-base and protonated were observed in Langmuir films depending on the pH of subphase. The complex comprised of merocyanine and Cu^{2+} or Co^{2+} metal ions are also able to form stable Langmuir films which compression isotherms are different from non-complex merocyanine. Also films composed of a mixture of merocyanine and fatty acid (eicosanoic acid) were prepared. Attractive and repulsive interactions between molecules in mixture films were observed. All types of the films were successfully transferred onto hydrophobic quartz plates for the purpose of producing solid samples of ultrathin sensors. Multilayers of free-base merocyanine films remain sensitive to the pH of the environment. From the changes in absorbance spectra of the merocyanine film it is possible to evaluate the pH of the microenvironment.

1. Introduction

The development of industrial civilization endangering the human environment has contributed to the continuous expansion of analytic controls and placed higher demands on measuring techniques. These demands can now be met due to the great progress in the development of various types of sensors.

The electronic spectra of the merocyanine are very sensitive to the changes in microenvironment [1–3]. Some of them are effective indicators of solvent polarity, pH, local electric field or transition metal ions strength [4,5]. It has been shown that these types of molecules readily incorporate into cell membranes, tumours and human tissues [6,7]. The merocyanine also has a great ability to form complexes with metal ions [8]. The ions of cobalt, copper and iron are present in high concentration in industrial areas and must be treated as a dangerous pollution of the environment. For this reason merocyanine dyes have attracted much attention for potential application in different types of sensors [9,10] and medical therapy [11].

In the previous study the changes of the electronic spectra of stilbazolium merocyanine in bulk solution at different concentration of cooper, cobalt and iron ions were investigated. The strong solvatochromic effect was observed [3,8,12]. Two forms of the merocyanine, free-base and protonated were observed depending on the pH of the solvent.

In this paper we report the study of Langmuir (L) and Langmuir–Blodgett (LB) films formed of stilbazolium betaine merocyanine 1-(12-hydroxydodecyl)-4-[(3-hydroxy-4-oxocyclohexa-2, 5-dienylidene)-ethylidene]-1,4-dihydropyridine (M20) and its mixtures with eicosanoic acid (AA). The complexes of M20 with metal ions (Cu^{2+} or Co^{2+}) were spread at the air–water interface. The form of merocyanine films was dependent on the pH of the subphase. The L films of free-base and protonated merocyanine form were successfully transferred onto hydprophobic quartz plates. The spectroscopic characterization was performed on the L and LB films. Chemical sensors can be made by use of Langmuir–Blodgett multilayer films of merocyanine that changes their optical characteristics when exposed to a particular chemical compound.

2. Materials and methods

Stilbazolium merocyanine 1-(12-hydroxydodecyl)-4-[(3-hydroxy-4-oxocyclohexa-2,5 dienylidene)-ethylidene]-1,4-dihydropyridine was synthesized and purified in the Institute of Physics at Poznan University of Technology by means of method described by Gruda and Bolduc [13]. The molecular structure of the merocyanine is presented in Fig. 1. The visible spectra were shown previously [3,8]. Eicosanoic acid was purchased from Sigma and used as sup-

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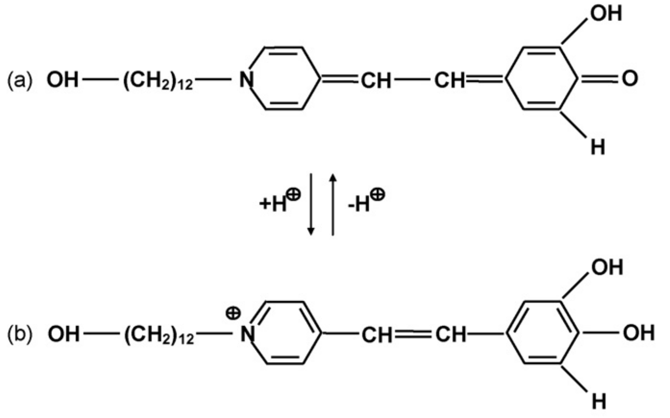

Fig. 1. Molecular structures of the merocyanine dye: (a) free-base form and (b) protonated form.

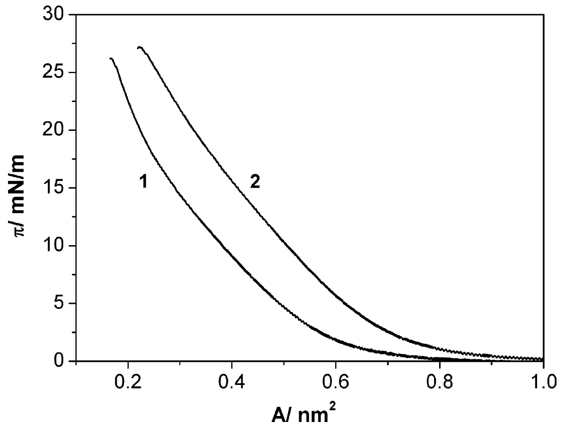

Fig. 2. π–A isotherms of pure M20 at the subphase of pH 3 (1) and pH 9 (2).

plied. Salts of transition metals: $Cu(CH_3COO)_2$ and $CoCl_2{\cdot}6H_2O$ were purchased from Fluka.

The merocyanine was dissolved in methanol and then introduced to the spectroscopic grad chloroform (Uvsole, Merck) at a concentration of 0.1 mM to obtain the stock spreading solution for Langmuir films experiments. In order to obtain merocyanine–metal complex the Cu or Co salt was added to a methanol solution of the dye. The two component spreading solutions were prepared as a mixture of appropriate volumes of the stock solutions of AA to produce the Langmuir films in a whole range of concentration of components.

In order to prepare the subphase for the Langmuir films two types of buffers were prepared:

(1) 0.2 M HCl + Mili-Q water; pH = 3
(2) 0.2 M HCl + 0.4 M Tris + Millie-Q water; pH = 9.

The Langmuir and Langmuir–Blodgett films were formed in a Minitrough 2 system from KSV Instruments (Finland). The dye and its two component mixtures were spread from freshly prepared chloroform stock solution onto the subphase surface of deionized water purified by Millipore system (Millipore S.A., France) or buffer of pH 3 or pH 9. The film was compressed symmetrically form both sides with a constant barrier speed of 5 mm/min. The Langmuir film was transferred onto a solid substrate by vertical deposition at constant surface pressure. The polished quartz plates (30 mm × 15 mm × 1 mm) with hydrophobized by hexamethyldisilazane (Fluka) surfaces were used. The L and LB experiments were performed at constant subphase temperature of 20 °C.

The absorption spectra of the bulk solutions and the LB films were recorded in the UV–vis region by means of Cary 400 spectrophotometer (Varian, Australia). A light guide accessory to Cary 400 and a trough with a quartz window at the bottom were used to record the absorption spectra of the dye directly form the surface of the subphase (*in situ* spectra).

3. Results and discussion

The merocyanine M20 is able to form a stable compressed monolayer at air–water interface. The surface pressure–mean molecular area (π–A) isotherms are presented in Fig. 2. A significant difference can be seen in a course of isotherm of the film compressed at the buffer of pH 3 (curve) and pH 9 (curve). The surface pressure π rises slowly from the mean area per molecule of 0.72 and 0.88 nm^2, respectively. The slope of isotherms is not high what suggest that the films are fragile and more compressible. More stable and less compressible is the film spread at the buffer of pH 9. In this case the free-base form of M20 should exist as suggested by the behavior of M20 in the bulk solution at pH 9 [3,8]. The film of M20 formed at the subphase of pH 3 should represent protonated form. The difference in the isotherm courses can be explained as a result of a higher electric dipole moment of M20 in the free-base form than protonated one [1]. Comparing the calculated surface of M20 molecule, taking into account the van der Waals radii of the atoms, with the mean molecular area occupied by M20 at the water interface we can assume that M20 molecules in free-base form lay flat at the water but the protonated molecules are tilted. Complexes comprised of M20 dye and Cu^{2+} or Co^{2+} ions are also able to form L films. The courses of compression isotherms for M20–Cu^{2+} and M20–Co^{2+} complexes were almost identical at the same buffer. The increase in π appears at almost four times larger area per molecule than for pure M20, as can be seen in Fig. 3. The films at the subphase of pH 9 were much stable than at the subphase of pH 3 what can be deduced from the slope of isotherms. The compressibility factor $c_S = -(1/A)(\partial A/\partial \pi)$ calculated at $\pi = 8$ mN/m for both L films of M20–metal ions are lower than for the films of M20. It is known that two molecules of merocyanine form complex with Cu^{2+} ion and the complex is stable [3]. In case of a complex with Co^{2+} four molecules are connected to one ion and the complex easy dissociate [3,8]. The main π–A isotherms parameters are gathered in Table 1 for comparison of the value of area per molecule A_0 when π begins to increase, A_{ext}—the value of area obtained by extrapolating the tangent of tilt angle of the π–A isotherm to $\pi = 0$ and the film compressibility factor c_S.

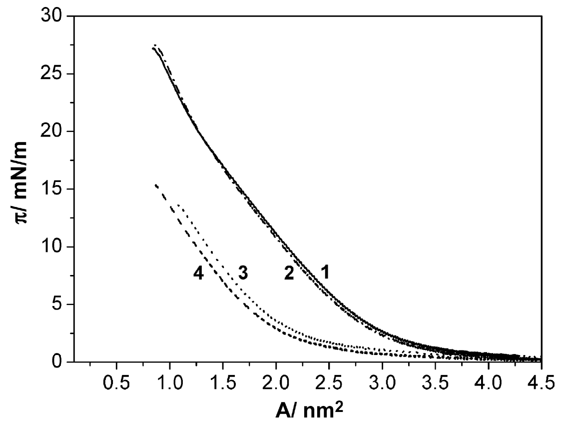

Fig. 3. π–A isotherms of M20–Co^{2+} complex (1) and M20–Cu^{2+} complex (2) at the subphase of pH 9, M20–Cu^{2+} complex (3) and M20–Co^{2+} complex (4) at the subphase of pH 3.