

Optical and photoelectrical properties of Langmuir-Blodgett diphthalocyanine thin films

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Langmuir-Blodgett films of tin diphthalocyanine (Pc_2Sn) were obtained. Films were prepared by consecutive transferring of Pc_2Sn monolayers from water surface on quartz or glass substrates by a Langmuir-Schaefer technique (the "horizontal lifting"). Absorption spectra of Pc_2Sn solid films compared to those of Pc_2Sn -solutions were thoroughly studied and discussed in the visible range of light spectrum. Spectral photo response correlates well with the film absorption in the whole spectral range studied that indicates the presence of photo electromotive force in Pc_2Sn films.

Методом Ленгмюра-Блоджетт получены пленки дифталоцианина олова (Pc_2Sn). Монослои формировались на поверхности воды после внесения раствора Pc_2Sn в хлороформе или хлорбензоле и переносились на стеклянную или кварцевую подложку по технологии Ленгмюра-Шеффера (или горизонтального "лифта"). Спектры поглощения пленок Ленгмюра-Блоджетт Pc_2Sn в сравнении со спектрами растворов вещества в хлороформе и хлорбензоле были изучены в широком спектральном диапазоне. Спектры fotocувствительности пленок Ленгмюра-Блоджетт и их спектры поглощения совпадают по форме во всем исследованном спектральном диапазоне, что свидетельствует о наличии фото-ЭДС в пленке.

1. Introduction

Phthalocyanines (Pc) belong to the class of macro heterocyclic organic compounds structurally related to porphyrins. Phthalocyanines are able easily to form chemical complexes with many metals of the periodic system of elements. Being possessed of high chemical stability, light resistance, and thermostability, phthalocyanines and their metal complexes have been historically widely used as synthetic dyes of green and sky blue colors [1]. Phthalocyanines of metals form, as a rule, molecular complexes that under optical excitation are characterized by charge transfer states. Absorption bands corresponding to those states are very sensitive to electrical field because of changes in dipole moments of molecular

centers absorbing light quanta. This dipole moment variation is easily detected by Stark spectroscopy technique [2, 3]. Many phthalocyanine metals exhibit semiconductor and photo-semiconductor properties [4]. Some of the phthalocyanine complexes possess macroscopic polarization and display polar (pyro- and even ferroelectric) properties [5, 6].

These specific properties of phthalocyanine complexes and formation of thin Pc films by different techniques give every possibility of using them in a wide scope of scientific and technical applications. Moreover, there is a trend to use thin Pc films in hybrid and hetero-thin film systems of different functional devices. Examples are information recording systems [7], electro-

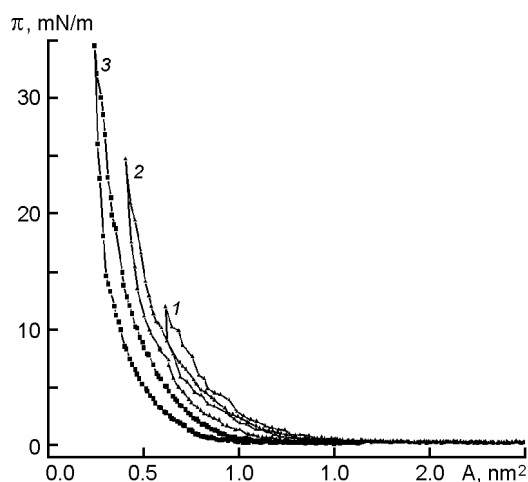


Fig. 1. The surface pressure vs. area per one molecule curve for PC_2Sn at different amounts of PC_2Sn solution (in chloroform) used for spreading onto water surface of Langmuir trough: curve 1 — 0.4 ml., 2 — 0.6 ml., 3 — 1 ml.

chromic materials [8], organic thin-film transistor (OTFT) [9], gas sensors [10].

In this work multimolecular films on the basis of insufficiently studied binuclear sandwich complex of tin diphthalocyanine (PC_2Sn) were prepared using Langmuir-Blodgett technique. Langmuir-Blodgett technology allow one to form multimolecular films of very low thickness comparable to a size down to one molecule. Some optical (absorption spectra), electro optical (Stark effect, photosensitivity) and dielectric properties of films of PC_2Sn were studied with the aim of further utilizing this material in different thin film heterosystem designs.

2. Experimental procedure

During the preparation of LB films, the behavior of monomolecular layer of PC_2Sn on a water surface was investigated. This was carried out to reveal the ideal conditions of the most homogeneous monolayer formation (elimination of aggregation effects and a local collapse). The isotherms of compression and monolayer stretching (dependence of surface pressure π on the area per one molecule A) have been studied at various amounts of PC_2Sn solution in chloroform volume (from 0.4 to 1.0 ml). Concentration of PC_2Sn solution was $c = 1.04 \cdot 10^{-2}$ wt %. Speed of barrier movement was $v = 0.04$ m/min. As seen in Fig. 1, at increased volume of a solution spread into a water surface, the surface pressure grows to its maximum

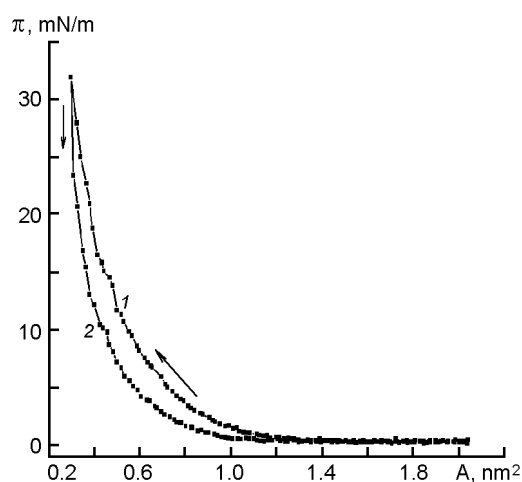


Fig. 2. The surface pressure vs. area per one molecule curve. Curve 1 — compression cycle, 2 — decompression cycle (volume of PC_2Sn solution in chloroform 0.8 ml.).

value (up to a collapse point). Simultaneously the area per one molecule decreases, the structure becomes more tightly packed. The estimated area per one phthalocyanine macrocycle is of $S_{\text{PC}} = 1.6$ nm^2 . The minimum value of the area a phthalocyanine macrocycle takes in a tightly packed structure is of $S_{\text{min}} = 0.35$ nm^2 .

In the plot of surface pressure dependence versus area per one molecule, Fig. 2, the areas, characterising a "gas" phase (pressure less than 0.5–1 mN/m), "liquid-expanded" (pressure of 1–12 mN/m), "condensed" (pressure over 12–15 mN/m) can be seen. At the pressure over 25 mN/m the condition close to collapsed state is observed. The area occupied by one PC_2Sn molecule in a "gas" phase, makes 1.5–1.6 nm^2 . The minimum value of the area occupied by one molecule in a tightly packed monolayer makes an area of 0.55 nm^2 , at extrapolation of the "condensed" phase to zero pressure. We outline that compression plot does not coincide with the curves of the films stretching. It can be explained by the aggregation of molecules in a monolayer lying on a water surface at high surface pressure values (we can observe the areas of temporary collapsed conditions on the π - A isotherms of PC_2Sn molecules). From these dependencies it is possible to calculate that PC_2Sn molecules are bend to the surface interface at an angle of $\theta \sim 77^\circ$ ($\cos\theta \approx 0.354$). Such behavior on a water surface is typical for molecules of phthalocyanines [10, 11].

Pc_2Sn monolayers transfer from water surface on solid substrates was carried out by a Langmuir-Schaefer method or the "horizontal lift". Pc_2Sn monolayers were formed after spreading Pc_2Sn chloroform solution onto the water surface by entering the solution of Pc_2Sn into chloroform with concentration $c = 7 \cdot 10^{-3} - 1.04 \cdot 10^{-2}$ wt %. Thin monomolecular films were compressed to the condition of tightly packed layers and then were consecutively transferred from the water surface onto quartz or glass substrates at the room temperature (293–300 K) and surface pressure $\pi = 7 - 9.5$ mN/m, pH = 6.0. The prepared tin diphthalocyanine films varied in thickness from 2 to 70 monolayers (3–105 nm).

3. Results and discussion

Phthalocyanine chromophore systems, containing the aromatic or heteroaromatic residuals and connected with each other by heteroatoms, are characterised by the presence of a system of conjugated bonds. The phthalocyanine chromophore system under study contains four pyrrol residuals which, together with four atoms of nitrogen connecting them form a heterocycle ("macrocycle"), i.e. a ring of alternating atoms of carbon and nitrogen [1–3]. Thus the heterocycle, being an equatorial ligand or some other ligand connected with the atom of metal, settle down itself a way of being perpendicular to the cycle planes (i.e. occupy transaxial position). Metals (M), as said above, are capable of formation of PCM type complexes or binuclear "sandwich" complexes of type Pc_2M . The structural formula of tin diphthalocyanine contains two phthalocyanine rings between which there is a tin atom connected by donor-acceptor bonds with eight atoms of nitrogen [4]. Eight atoms of nitrogen in every phthalocyanine macrocycle together with atoms of carbon form a pyrrol ring. In a peripheral part of molecules there are four benzene rings, in each of which one of the hydrogen atoms may be replaced by group R (substituted phthalocyanines). In our case the role of R is played by the atom of hydrogen.

Tin diphthalocyanine Pc_2Sn spectra have been measured earlier in solutions of chlorobenzene [4], dimethoxyethane and chloronaphthalene [5]. Spectral characteristics of a variety of phthalocyanine derivatives are summarized in [6]. In work [4] it has been shown that the spectrum of Pc_2Sn compound in chlorobenzene consists of an intensive band

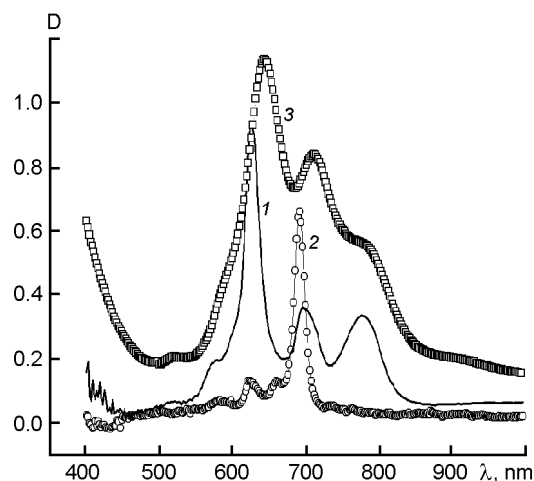


Fig. 3. Absorption spectra of Pc_2Sn in different solutions: 1 — chlorbenzol; 2 — chloroform; and 3 — absorption spectrum of solid Pc_2Sn Langmuir-Blodgett film.

at the wavelength $\lambda_{max} = 628.5$ nm and the widened band $\lambda_{max} = 770$ nm. Such kind of a spectrum has been explained by interaction between phthalocyanine macrocycles.

Spectra of absorption of solid LB films of tin diphthalocyanine compared to those of some Pc_2Sn -solutions have been measured in the visible light range. In Fig. 3 the Pc_2Sn absorption spectra are presented in the range of 400–1000 nm: for tin diphthalocyanine solutions in chlorobenzene ChB (curve 1), for the solution in chloroform ChF (curve 2), and for a solid Pc_2Sn LB film of 35 layers in thickness, which has been prepared using diluted solution of Pc_2Sn in ChF (curve 3). According to the curves spectra, the character of absorption spectra of Pc_2Sn solutions in ChB and ChF are identical, though the shift of the Q-band towards the shorter wavelengths in case of Pc_2Sn solution in ChB in comparison with that of the solution in ChF is clearly observed. That can be explained by the individual molecular interaction between the solvent molecules of different nature and ligand reactive species incorporated into phthalocyanine macrocycle.

The absorption spectra of Pc_2Sn in ChB solvent (Fig. 3) compared with the literature data [4] are turned out to be the same: for both cases the values of absorption maxima are in good agreement. So, for instance, one can see from the Figures that $\lambda_0 = 350(338)$ nm (B-band), $\lambda_1 = 577(575)$ nm, $\lambda_2 = 625(626)$ nm (Q-band), $\lambda_3 = 698$ nm, $\lambda_4 = 779(774)$ nm, in brackets values of maxima taken from work [4] are given. Note that spectrum of

the solid Langmuir film of Pc_2Sn , is clearly distinguished from the spectra of Pc_2Sn in the solutions. This specific behavior is a fundamental character of the absorption process in the tightly packed structure of the solid film, in comparison with that in Pc_2Sn solutions. As a result, the widened basic Q -band has practically been merged with the other characteristic maxima. We have carried out also an investigation of Pc_2Sn LB films absorption spectra in wider wavelength range (from UV to IR).

In Fig. 4 the absorption spectrum of Pc_2Sn LB film in the range of 250–2000 nm (curve 1) is presented. Here we again observe a number of bands Q (790 nm, 700 nm, 650 nm, 520 nm); B -Sorrel band (350 nm), N (290 nm), L (around 230 nm). The nature of these bands is well known [5, 6]. Long-wave band Q is caused by electronic transition $a_{1u}-e_g$, orbital transition a_{1u} is localized mainly on α -carbon atoms of pyrrol fragments, the basic orbital transition e_g is delocalized on both macrocycles of diphthalocyanine molecules. B -band (Sorrel) in UV area of 350 nm is caused by transitions $a_{2u}-e_g$, a_{2u} orbital transition is localized on bridge atoms of nitrogen. In the UV region the observed N -, L -, C -bands can be explained with the transition $b_{2u}-e_g$, where b_{2u} orbital transition is localized on pyrrol atoms of nitrogen. Bands B , N , L are shown also to be present in the spectra of Pc_2Sn LB films. Besides, in the IR region one can distinguish the local absorption maximum near the wave length of about 1400 nanometers which can be attributed to the charge transfer effect between two phthalocyanine rings [15].

The spectra of photosensitivity of LB films in wide spectral range of 260–1800 nanometers were studied as well. Photo-response (photosensitivity) of the films was measured by two technique: by synchronous detecting at the frequency of 80 Hz with the use of virtual PC programs PhysLab (by Palto) and with the use of current-voltage transducer (for dc current mode of operation and for very low modulation frequencies). The xenon lamp DKSSH-150 was used as a light source. Its spectral dependence of flux intensity was defined by the calibrated silicon photo diode. Measurements in the 1000–2000 nm spectral region were made of with the use of PbS photoresistor. Spectral studying of photosensitivity of Pc_2Sn films have shown that normalized spectra of absorption and photosensitivity of the

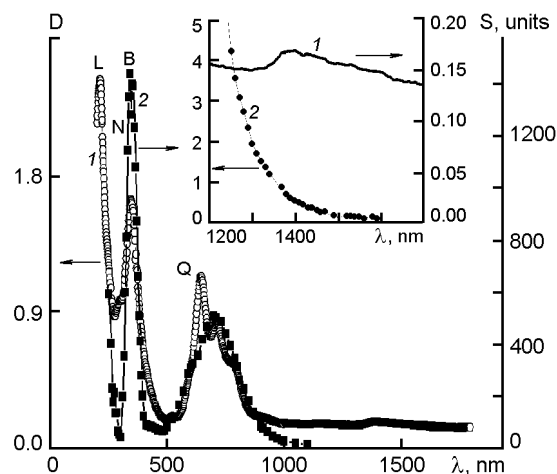


Fig. 4. Absorption spectrum of Pc_2Sn Langmuir-Blogett film (thickness 35 monolayers) (curve 1), photosensitivity spectrum (curve 2) in wavelength range of 260–1800 nm. The inset — absorption spectrum (1) and photosensitivity spectrum (2) in larger scale 800–1600 nm.

Pc_2Sn films are identical. Electromotive force (EMF) signal (in dc mode) was of about a few mV.

4. Conclusion

Thus, we have investigated the behavior of monolayers of Pc_2Sn molecules on the water surface. π -A isotherms of surface pressure dependences for Pc_2Sn molecules were thoroughly studied. Langmuir-Blodgett films on the basis of Pc_2Sn were prepared with the film thickness varied from two to 70 monolayers (3–105 nm). Absorption spectra of Pc_2Sn LB films and Pc_2Sn in organic solvents were studied. Photosensitivity spectra of LB Pc_2Sn films in the range of 260–1800 nm revealed that they are completely defined by the spectral absorption of the chromophore system of the diphthalocyanine dye.

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References

1. B.D. Berezin, Coordination Compounds of Porphyrins and Phthalocyanines, Science, Moscow (1978) [in Russian].
2. B.I. Stepanov in: Chemistry and Technology of Organic Dyes, Chemistry, Moscow (1984) [in Russian].

3. Porphyrins: Spectroscopy, Electrochemistry, Application, Under the Editorship of N.S.Enikolopjana, Nauka, Moscow (1987).
4. M. Whalley, *J. Chem. Soc.*, 866 (1961).
5. L. Edwards, M. Gouterman, *J. Mol. Spectr.*, **33**, 292 (1970).
6. Electronic Spectra and Related Connections, the Catalogue, Under the editorship of Prof. Lukjantsa E.A, Moscow Research-and-Production Association, Branch of Scientific Research Institute of Technical and Economic Researches (Cherkassy), Cherkassy (1989), v.94.
7. W. Hu, Y. Liu, Y. Xu et al., *Synth. Met.*, **104**, 19 (1999).
8. N. Nensala, T. Nyokong, *Polyhedron*, **15**, 867 (1996).
9. Lijuan Zhen, Liwei Shang, Ming Liu et al., *Appl. Phys. Lett.*, **93**, 203302 (2008).
10. A. Zlatkin, S. Yudin, *Advan. Mat. Opt. . Electr.*, **5**, 259 (1995).
11. N.L. Levshin, G. Yudin, E.A. Krylov, A.T. Zlatkin, *Phys. Chem. Mag.*, **82**, 1 (2008).
12. S. Yudin, L. Blinov, N. Petuhova, S. Palto, *Techn. Phys. Lett.*, **70**, 626 (1999).
13. S.P. Palto, A.V. Sorokin, A.A. Tevosov, S.G. Yudin, *Opt. Spectr.*, **98**, 627 (2005).
14. N.L. Levshin, N.N. Pronin, P.A. Forsh, S.G. Yudin, *Phys. Techn. Semicond.*, **48**, 199 (2008).
15. L.M. Blinov, G. Grewer, M. Loesche et al., *Mol. Mat.*, **2**, 127 (1993).

Оптичні і фотоелектричні властивості плівок Ленгмюра-Блоджетт дифталоціаніна олова

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Методом Ленгмюра-Блоджетт отримано плівки дифталоціаніна олова (Pc_2Sn). Моношари формувалися на поверхні води після внесення розчину Pc_2Sn у хлороформі або хлорбензолі і переносилися на скляну або кварцеву підкладку за технологією Ленгмюра-Шефера (або горизонтального "ліфта"). Спектри поглинання плівок Ленгмюра-Блоджетт Pc_2Sn/Pc_2Sn порівняно із спектрами розчинів речовини у хлороформі і хлорбензолі вивчено в широкому спектральному діапазоні. Спектри fotocутливості плівок Ленгмюра-Блоджетт та їх спектри поглинання співпадають за формою у всьому дослідженому спектральному діапазоні, що свідчить про наявність фото-ЕРС у плівці.