

CHARACTERISTICS OF LANGMUIR BLODGETT FILMS OBTAINED FROM NEW PHTHALOCYANINE DERIVATIVES

A. Dragan *, Otilia Cinteza ** and V. Magearu *

abstract: Surface activities, including self-assembling properties as monolayers and multilayers at gas-liquid and solid-gas interfaces were investigated for some metallic phthalocyanines derivatives. Phthalocyanine compounds with Cu and Sm, and various substituted hydrophobic and hydrophilic groups were investigated, in order to determine the monolayer forming and deposition Langmuir Blodgett films behaviour. Particular attention was given to films containing Sm derivatives, which is described as a compound with many potential applications in sensor devices.

Introduction

The growing interest in the use of phthalocyanine compounds in the production of miniaturized electronic devices able to act as chemical and biochemical sensors is due to their capacity to satisfy a large number of optical and electrical requirements. Another major advantage is the remarkable chemical and thermal stability of the phthalocyanine derivatives.

From the large scale of applications it is to remind the ones from the biomedical field, such as in photodynamic cancer therapy, e.g the fluoraluminium phthalocyanine used as a targeting molecule in anticancer treatment, in plastic surgery and immunology (e.g detection of very low levels of some metallic ions and organic compounds in blood, biological fluids, serum and urine) and “in vivo” applications where are used to eliminate plague bacteria from a carious lesion. In the same time, the phthalocyanine compounds are successful used in construction of modified electrodes for determination of very low concentrations of organophosphoric and organocarbamate pesticides.

Samarium phthalocyanine is one of the most promising organic materials to be used in various devices. Its nonlinear optical properties, photoconductivity and chemical stability confer a solid motivation of the great potential for applications as a main component in photoreceptors, sensors, solar cells and electroluminescent devices, optical disks, in photodynamic therapy of cancer, electronic photography, electronic printing. For the majority of applications the highest efficiency of the material is achieved in highly ordered films.

* Department of Analytical Chemistry, University of Bucharest, Sos.Panduri 90-92, 050657, Bucharest, Romania

** Department of Physical Chemistry, University of Bucharest, Regina Elisabeta Blvd. 412, 030018, Bucharest, Romania, e-mail ocinteza@gw-chimie.math.unibuc.ro

High vacuum deposition method leads to the formation of evaporated films with various properties, which is dependent on the preparation conditions. If the slow deposition speed and the lack of reliability (as major obstacles) could be removed, the Langmuir-Blodgett (LB) technique would be the technique of choice.

Some papers [1-3] report studies on the Langmuir-Blodgett films preparation from various unsubstituted phthalocyanine derivatives. Adequate monolayers at the W/A interface, able to promote the formation of organized LB films can be obtained by the attachment of hydrophilic and/or hydrophobic substituents to control the molecule-water interaction. Usually, changes in chemical structure lead to severe modification of all properties, including specific targeted properties, such as photoconductivity and nonlinear optic properties. A different strategy is to mix the phthalocyanine derivative with some other compound with known film-forming properties. The method was proposed by Kuhl and Mobius [4 -6] using fatty acids as matrixes.

The aim of the present study is to prepare LB films from some new metallic substituted phthalocyanine compounds with promising optical and chemical properties.

Experimental

Materials

The phthalocyanine derivatives used in this study were aminated compound substituted with various alkyl chains and various metals.

The general chemical structure was:

Compound 1 (Cu PC1):

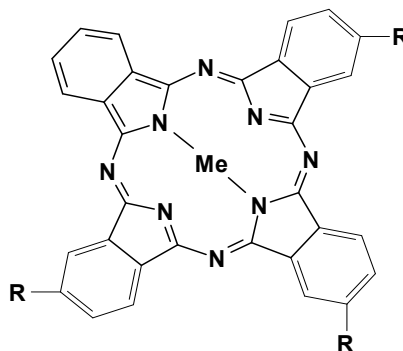
R = -CH₂-NH-CH₂-CH₃; Me = Cu

Compound 2 (Cu PC2):

R = -CH₂-NH-(CH₂)₁₁-CH₃; Me = Cu

Compound 3 (Sm PC):

R = -CH₂-NH-CH₂-CH₃; Me = Sm



The aminated derivatives were prepared as laboratory samples and used without further purification. The preparation of long alkyl chain phthalocyanine with Cu and the one with Sm investigated in this study and their characterization were described elsewhere [7].

The parent underivatized molecule of metal phthalocyanine with Cu (reagent from Sigma) was used as a reference compound.

Geometric characteristics of the phthalocyanine molecules were calculated from data on van der Waals atomic radii and using molecular dynamic programs.

Langmuir Blodgett films preparation

Thin films from pure phthalocyanine compounds and their mixtures with long chain amphiphiles were obtained by deposition onto glass and silica solid surfaces. The monolayers at the air-water interface were transferred as Langmuir Blodgett films by using different techniques. For preparation, the glass slides and silica hydrophobized supports are carefully cleaned before the film deposition with reported procedures. Typical deposition techniques are used (vertical movement of the plate) but angles other than 90° have been used successfully (tilted method).

Surface Isotherms

Surface pressure isotherms were determined by Wilhelmy plate method, using a thermostated Langmuir trough and a platinum microplate Kruss. The accuracy of the method was 0.1 mN/m.

All measurements were made on monolayers spread on water with resistivity about 18 mΩ cm. The water was previously subjected to purification through a reverse osmosis system equipped with two deionising cartridges and a 0,22 μm filter.

The compounds were transferred onto the water surface as solutions in various solvents. As spreading vehicles some uncommon mixtures were used, because the poor solubility of phthalocyanine derivatives: xylene-tetrahydrofuran (5:1), toluene-1,1,1-trichloroethane, toluene-tetrahydrofuran, toluene-chloroform, toluene-dichloromethane, xylene-1,1,1-trichloroethane, etc. The most suitable solvents were found to be dichloromethane and toluene-dichloromethane.

Surface pressure isotherms were recorded after 30 minutes after spreading procedure. The aggregation and crystallisation during the evaporation process was checked visually.

The contact angles were measured in dynamic regime during deposition and in the static regime as advancing and receding angles with a video capture device and computer analysis of the shape of the interfaces. Because both the solid substrates are very hydrophilic a reverse method was used (gas bubbles deposited onto the solid surface within the liquid phase were analysed).

The UV-VIS spectra were recorded both in solutions and in LB films using a Jasco series V650 spectrophotometer.

Results and Discussions

The specific surface of the molecule occupied in the water/air interface was calculated and compared with data obtained from surface pressure isotherm. Both this data and the stability of the phthalocyanine monolayers at water/air interface are shown in Table 1.

One can presume that the phthalocyanine molecules are oriented parallel to the surface, due to the similar values of the theoretic values and experimental specific surface area per molecule in the W/A interface.

Table 1. Stability of the phthalocyanine monolayers at W/A interface

No	Compound	A ($\text{\AA}^2/\text{molec}$) vs calculated A	Stability (%)
1	CuPC1	109/102	7
2	CuPC2	123/135	9
3	SmPC	115/110	10

Some usual equations were used to fit the experimental data of bidimensional pressure isotherms at air-water interface for simple and mixed systems with phthalocyanines. The well known equation of state for monolayers at W/A interface fit adequate the experimental data but they not offer phenomenological interpretation of the changes in molecular interactions. Ruckenstein-Li equation [8] was used in order to give a more detailed analysis of the relationship between chemical structure and the molecular interaction in interfacial monolayer.

$$(\Pi + kTP)(A - A_0) = kT \quad (1)$$

where the second term is defined as:

$$kTP' = \frac{\partial(\Delta f)^0}{\partial A} \quad (2)$$

and is considered as surface cohesion pressure correction term. Surface cohesion pressure is involving contributions due to: the polar interactions (α_p), the chain van der Waals interactions (α_v) and the chain conformation (α_c)

For the W/A monolayer:

$$\frac{\Pi A_0}{kT} = -\ln(1-\rho) + (\alpha_p + \alpha_v) \left(\frac{T_0}{T}\right) \rho^2 + 2\alpha_c \rho^3 \quad (3)$$

The equation (3) reflects contribution of polar interactions, van der Waals interactions and chain conformation to the surface cohesion pressure in various phthalocyanine compounds and the mixture with stearic acid. The values for interaction parameters for phthalocyanine monolayers are given in Table 2.

Table 2. Interaction parameters in Ruckenstein-Li equation for phthalocyanine monolayers

No	Monolayer	α_p	α_v	α_c
1	CuPC1	14.10	-4.14	7.88
2	CuPC2	12.06	-18.32	13.14
3	SmPC	19.80	-3.20	6.50
4	SmPC-stearic acid	10.12	-12.88	2.87

Langmuir- Blodgett films were prepared from different phthalocyanine derivative by deposition on glass as solid substrate. The details of the deposition procedure and the characteristic of the LB films on the glass slides are summarized in Table 3.

Table 3. Langmuir Blodgett films for Cu and Sm phthalocyanine compounds.

No	Compound	Dipping speed (cm/s)	Deposition type	Transfer ratio
1	CuPC1	0.04	Z	50
2	CuPC1	0.03	Z	>55
3	CuPC2	0.04	Y	63
4	CuPC2	0.03	Y	74
5	SmPC	0.05	Y	56
6	SmPC	0.03	Y	62

Although no quantitative intensity measurement was made, the Bragg intensity was much weaker than that found for the LB film made from stearic acid. This suggests that only a small part of each film is obtained as ordered multilayers parallel to the substrate surface.

The spread and the efficiency of the deposition, as measured of the transfer ratio, are closely related to the dynamics of the three phase contact line and the dynamic contact angles. For low immersion and removal speeds (10^{-4} - 10^{-2} m/s) dynamic contact angles are very similar to the static advancing and static receding contact angles. Following Huhl and Scriveen's convention, during immersion dynamic contact angles are measured in the liquid phase, while during removal contact angles are measured in the air phase.

To characterize the deposition and the order of monolayer transferred onto the silica and glass supports, the static contact angles were measured. Contact angle ϕ is the angle measured for the gas bubble (complement of conventional θ angle of water on the solid substrate). The results are summarized in Table 4.

Table 4. Static advancing contact angles for the monolayers of phthalocyanine deposited on glass substrate.

No	Compound	Contact angle / 1 layer	Contact angle /10 layers
1	CuPC1	186	183
2	CuPC2	167	152
3	SmPC	187	185
4	SmPC-stearic acid	140	131

Optical properties of the phthalocyanines were investigated, both in solution and in thin films. Obtained UV-VIS spectra for the solution of various phthalocyanine compounds are shown in Fig. 1.

The change of alkyl chain length does not affect the spectra of the phthalocyanine. The absorption maxima at 677 nm and 647 nm is the phthalocyanine Q-band due to the transition from the split π (a_{2u}) orbitals to the upper π^* (eg) orbitals.

The absorbance recorded for the LB film deposited on glass show that as the number of layers increases the absorbance follow the Beer's law.

The LB film deposited on glass is red-shifted with respect to the solution spectra. The red shift can be attributed to head to tail arrangement of the dipoles, which results in J-type aggregates [9,10] as it is shown in Fig. 2, where is presented the behaviour of the film deposited from mixed monolayers Sm PC-stearic acid.

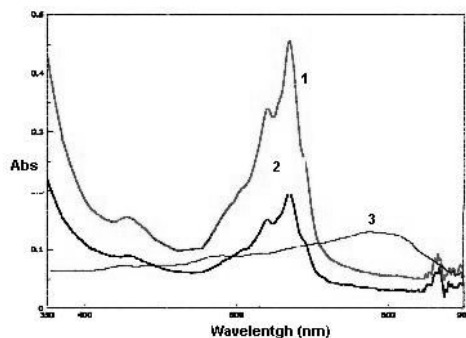


Fig. 1 Electronic absorption spectra of the phthalocyanine compounds (1: Cu PC2, 2- Cu PC1, 3- Sm PC2).

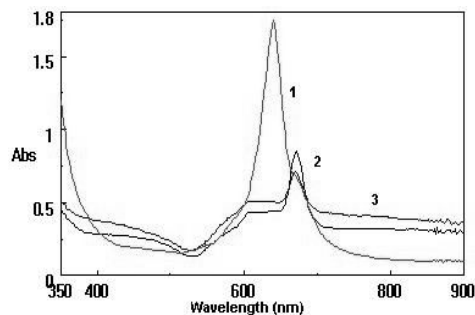


Fig. 2 Absorption spectra of Sm PC derivative in solution (2), in LB film – 40 layers deposited (3) and in LB mixed film with stearic acid (1). The absorption spectra for LB films are represented in arbitrary units.

The mixed films exhibit a high intensity absorption band centred around 800 nm. The spectrum is similar in profile to that of the film obtained in high vacuum deposition, characterized by a low degree of ordering. The behaviour is similar with that reported for some other macrocyclic dye in mixed films [11,12]. The presence of the fatty acid molecules seem to fill in the spaces between the dye molecules, preventing molecular stacking and facilitating the interfacial orientation of the phthalocyanine.

CONCLUSIONS

Surface activity, including self-assembling properties as monolayers and multilayers at gas-liquid and solid-gas interfaces was investigated for some metallic phthalocyanine derivatives.

Phthalocyanine compounds with Cu and Sm, and various substituted hydrophobic and hydrophilic groups were investigated, in order to determine the monolayer forming and deposition Langmuir-Blodgett films behaviour. As expected, the Copper phthalocyanine substituted with dodecyl hydrocarbon chain show the best monolayer behaviour at the air-water interface, forming a flexible and coherent film that can be deposited onto solid substrate.

For the more hydrophilic compounds, which form rigid films, or no stable film, the behaviour of the phthalocyanine compounds in their mixture with phospholipids and stearic acid was investigated.

Some usual equations were used to fit the experimental data of bidimensional pressure isotherms at air-water interface for above simple and mixed systems with phthalocyanines.

Thin films from pure phthalocyanine compounds and their mixtures with long chain amphiphiles were obtained by deposition onto glass and silica solid surfaces. The monolayers at the air-water interface were transferred as Langmuir Blodgett films by using different techniques.

The composition and the degree of ordering in phthalocyanine films have been investigated using UV-VIS spectroscopy and contact angle measurements. Examples of the mixtures phthalocyanine-long chain alkyl surfactants are excellent for fabrication of Langmuir Blodgett films, giving evenly deposited well ordered multilayer assemblies by Y or Z type deposition. The homogeneity property of the Langmuir Blodgett films deposited onto solid surface from monolayers in various states were investigated in order to determine the most suitable surface pressure of the monolayer to be used.

Particular attention has been given to films containing Sm derivatives, which is described as a compound with many potential applications in sensor devices. The mixed film shows a non-ideal mixing behavior, suggesting an interaction in interfacial layer between the fatty acid and phthalocyanine molecules.

The possibility to obtain highly ordered monolayers at the air-water interface in mixed systems with Sm phthalocyanine derivatives should appreciably extend the utility of the new Sm derivative in Langmuir-Blodgett films obtained with various transferred techniques.

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