Features of formation of Langmuir monolayers of porphyrin derivatives on the surface of aqueous solutions of copper nanoparticles

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Abstract. Meso-aryl-substituted porphyrin monolayers were obtained by the Langmuir method depending on the aliquots applied to the water surface and the composition of the subphase. Regardless of the composition of the subphase (pure water or a solution with copper nanoparticles stabilized by surfactant) porphyrin compression isotherms showed the formation of monolayers until a film collapse state is reached. The presence in the subphase volume of copper nanoparticles stabilized by a surfactant (sodium dodecyl sulfate) contributed to the formation of a more stable porphyrin monolayer. A significant difference in the values of the surface potential at the end of porphyrin monolayer compression depending on the composition of the subphase is established. This fact is very promising in the context of creating film heterostructures with improved operational properties.

1. Introduction

In recent years, much attention has been paid to the synthesis of new photosensitizers based on porphyrins and their derivatives [1, 2]. Such compounds have a certain chemical activity and the ability of supramolecular organization in solution, which is confirmed by many spectroscopic methods [3]. In addition, the incorporation of certain metal atoms into the molecule is the reason for the manifestation of various optical effects, in particular, to an increase of radiative and nonradiative intercombination transitions, which lead to quenching of fluorescence and a decrease of the duration of phosphorescence [4]. Such electronic effects make these substances very attractive for practical use in optical systems as chromophores and phosphors with controlled parameters.

In order to include such substances in various modern film technological methods (such as the technology of creating chips for microelectronics, bio- and chemical sensors, optical devices, chip-on-lab systems, etc.), it is important to obtain layers with high ordering. Moreover, the ability to control their structure or physicochemical properties by a varying any external conditions is especially important. The Langmuir method is suitable to solve these problems. It allows one to order monolayers of amphiphilic molecules at the gas-water interface by the principles of self-organization.
of amphiphilic molecules [5, 6, 7]. This method allows to obtain a single-component and multicomponent films with a given structure, physical and optical properties and controlled thickness. The mutual influence of the components is characteristic of multicomponent systems [8, 9].

Interactions in film systems are of particular interest. Many authors describe various effects in such monolayers [10, 11]. For example, the formation of their own monolayers of porphyrins, or when it is present in a mixture with organic amphiphilic matrices. The intramolecular incorporation of metal ions and other molecular transformations are also described. In this case, the mixture, which is initially homogeneous in solution, can separate into separate phases on the water surface [12], and can interact with components dissolved in the subphase [13]. All this once again confirms the complexity of the issue that we tried to consider in this paper.

The main purpose of this work was to study the features of the formation of meso-aryl substituted porphyrin monolayers on the surface of aqueous solutions of copper nanoparticles (Cu NPs) stabilized by sodium dodecyl sulfate (SDS) surfactant.

The work was divided into several stages. Initially, the synthesis of nanoparticles was carried out. Then, preliminary studies were carried out with a variation of the volume (aliquot) of applied porphyrin, and its optimal value was determined. At the last stage, the effect of Cu NPs on the formation of porphyrin Langmuir monolayer upon the introduction of nanoparticles into the subphase was studied.

2. Materials and methods
An amphiphilic porphyrin 5,10,15,20-tetrakis(4-hexadecyloxyphenyl) (Ia-16) was synthesized by method described in [14]. Langmuir monolayers were formed by applying a solution of porphyrin in chloroform (5×10−4 M) to the surface of ultrapure water purified by Smart2Pure from Thermo Scientific (18.2 MΩ×cm) and an aqueous solution containing Cu NPs stabilized by SDS surfactant. The subphase with Cu NPs was prepared by adding 500 μl of a colloidal solution of Cu NPs stabilized by SDS surfactant into water with a volume of 150 μl. A colloidal solution of Cu NPs was obtained by the method described in [15, 16, 17]. Surface pressure–monolayer area (π–A) and surface potential–monolayer area (∆V–A) isotherms were obtained on the KSV NIMA LB Trough Medium KN 2002 (KSV Instruments Ltd., Finland) with the KSV NIMA Surface Potential Sensor for measuring surface potential. Surface tension was measured by weighing a Wilhelmy plate at a subphase temperature of 23 °C. The time for evaporation of the solvent and the uniform distribution of molecules on the water surface was 5 minutes. After monolayer was compressed symmetrically from both sides at a barrier motion speed of 20 mm/min. The influence of Cu NPs in the subphase on the stability of the porphyrin monolayer formed was evaluated by compressing the monolayer to a close-packed state (up to a surface pressure of 45 mN/m). At this pressure the relaxation of the monolayer area was studied.

3. Results and discussion
Figure 1 shows the π–A isotherms of porphyrin monolayers at the air-water interface depending on the aliquots of the deposited solution (V0). The inset in Figure 1 shows the molecular structure of the studied meso-aryl-substituted porphyrin. The parameters of the monolayer were determined from the compression isotherms. By extrapolating the linear sections of the isotherms to the axis A (π = 0), we determined the area Aex occupied by the monolayer in the condensed state (specific area). The mechanical properties of a monolayer as compressibility δ and compression modulus χ were determined from equations (1) [18]:

\[
\delta = \frac{1}{A} \left( \frac{dA}{d\pi} \right)_{T=\text{const}} ; \quad \chi = \frac{1}{\delta},
\]

where, A and dA are the specific area and its differential, d\pi is the differential of surface pressure.

Parameters of monolayers are given in Table 1.

It can be seen that with increase of the porphyrin solution aliquots the isotherms shift toward large specific areas. Moreover, the monolayer obtained by applying 10 μl is in the gas state. This volume of
substance is not enough to form a close-packed monolayer. At 50 μl, a transition to a liquid-expanded state is observed. However, monolayer collapse is achieved only with aliquots of 100 μl and 150 μl at a surface pressure of 70 mN/m. Also, an increase of the aliquots volume from 100 μl to 150 μl leads to increase of the specific area per monolayer by 21%. In this case, the compressibility of the monolayer decreases, and the compression modulus increases by no more than 1.6 times.

![Graph](image)

**Figure 1.** π-A isotherms of porphyrin with different aliquots applied to the surface of pure water. The insert shows a meso-aryl-substituted porphyrin molecular compound.

**Table 1.** Parameters of the porphyrin monolayer (area $A_{ex}$, compressibility $\delta$, compression modulus $\chi$ of monolayer) in the condensed state with different aliquots applied to the surface of pure water.

| $V_{al}$, μl | $A_{ex}$, cm$^2$ | $\delta$, m/mN | $\chi$, mN/m |
|--------------|-----------------|----------------|-------------|
| 50           | 38,8            | 0,0849         | 11,8        |
| 100          | 74,9            | 0,0286         | 34,9        |
| 150          | 94,5            | 0,0181         | 55,2        |

Porphyrin monolayers were studied on the surface of an aqueous solution containing Cu NPs stabilized by SDS surfactant with an optimal aliquot of 100 μl. Figure 2 shows the isotherms obtained for the individual components (porphyrin and Cu NPs stabilized by SDS surfactant on the pure water) and a mixed monolayer. Parameters of monolayers are given in Table 2.

Studies show that the addition of nanoparticles to the subphase reduces the specific area per porphyrin monolayer in the condensed state by 9.2 %, and an increase the compressibility of the monolayer by 1.2 times. Isotherms show the conservation of condensed phases without collapse up to 65 mN/m.

A significant difference of the values of the surface potential at the end of the porphyrin monolayer compression is established. There are 94 mV of the monolayer formed on the surface of pure water and 903 mV of the monolayer formed on the surface of the subphase containing Cu NPs stabilized by SDS surfactant. This fact is very promising in the context of creating heterostructures films with improved operational properties. A similar behavior was observed in [19, 20]. They explained the decrease of the area per monolayer in the condensed state based on the probable oblique orientation of the porphyrins at the air-water interface.

Explaining the results of our experiment, we can assume that the hydrophobic surfactant fragments penetrating at the air-water interface surrounding the copper particles contribute to the perpendicular orientation of the alkoxyl substituents of the porphyrin compound relative to the phase boundary. Thus, there is a decrease of the area per molecule in the layer and, accordingly, the specific area per monolayer. To finally resolve this question, we plan to carry out additional research.
Figure 2. $\pi$-A isotherms for Langmuir monolayers of porphyrin on water (1) and an aqueous solution of Cu NPs stabilized by SDS (2) and for Gibbs monolayer of Cu NPs stabilized by SDS (3).

Table 2. Parameters of the porphyrin monolayer (area $A_{ex}$, compressibility $\delta$, compression modulus $\chi$ of monolayer) in the condensed state on the surface of pure water and an aqueous solution containing of Cu NPs stabilized by SDS surfactant.

| Monolayer/subphase | $A_{ex}$, cm$^2$ | $\delta$, mN/m | $\chi$, mN/m |
|--------------------|-----------------|----------------|---------------|
| Ia-16/H$_2$O       | 74,6            | 0,02924        | 34,2          |
| Ia-16/H$_2$O+Cu NPs| 68,8            | 0,03403        | 29,4          |

Figure 3 shows an increase of the porphyrin monolayer stability in the presence of Cu NPs stabilized by SDS surfactant in the subphase relatively pure water. At a surface pressure of 45 mN/m, the porphyrin monolayer loses 21 % of its area for 120 minutes on water. On an aqueous solution with Cu NPs, the area loss at a given time is 13 %. We can also explain the effect of increasing the monolayer stability by the incorporation of hydrophobic surfactant fragments into the hydrophobic region of the monolayer formed by the alkoxyyl substituents of the porphyrin derivative at the phase boundary. This is also due to their mutual orientation, which leads to the compaction of the monolayer as a whole.

Figure 3. Relaxation curves of porphyrin monolayers on the surface of pure water (black curve) and on an aqueous solution containing Cu NPs stabilized by SDS surfactant (red curve).
To analyze the properties of the porphyrin monolayer formed on an aqueous subphase containing Cu NPs stabilized by SDS surfactant, we recorded $\pi$-$A$ and $\Delta V$-$A$ isotherms for both individual substances (Figure 4, a and b), and for mixed composition (Figure 4, c). In both cases (Figure 4, a and c), behavior and parameters of the compression isotherms of the porphyrin monolayer do not change in relation to each other. This indicates that the compression process on both subphases leads to a similar behavior in terms of the location of the porphyrin molecules in the monolayer.

![Figure 4](image)

**Figure 4.** $\pi$-$A$ (black curve) and $\Delta V$-$A$ (blue curve) isotherms for (a) Ia-16/H$_2$O, (b) H$_2$O+Cu NPs, (c) Ia-16/H$_2$O+Cu NPs monolayers.

The situation is completely different with the surface potential of the monolayer of the porphyrin derivative in the cases of presence or absence of Cu NPs stabilized by SDS surfactant in the subphase (Figure 4, a and c). There is a significant difference of the values of the surface potential at the end of porphyrin monolayer compression. When a porphyrin monolayer is formed on the surface of water $\Delta V$ is equal to 94 mV, and on the surface of a subphase containing Cu NPs stabilized by SDS surfactant $\Delta V$ is equal to 903 mV. This fact is very interesting in the context of creating heterostructures films with improved performance properties. Establishing a mechanism for such an almost tenfold increase of surface potential requires additional research.

4. **Conclusions**

The meso-aryl-substituted porphyrin can form Langmuir monolayers at air-water interface. The isotherms show a shift of the curves toward large specific areas per monolayer with an increase of the porphyrin solution aliquots applied to the subphase. In this case, the compressibility of the monolayer decreases. Upon modification of the porphyrin monolayer by Cu nanoparticles stabilized by SDS surfactant, its stability is increased relative to pure porphyrin. A significant difference of the surface potential values at the end of the porphyrin monolayer compression on the subphase containing Cu NPs stabilized by SDS surfactant relatively pure water requires further research.
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