Study of Langmuir monolayers and Langmuir-Schaefer films based on symmetrical meso-aryl-substituted porphyrin derivative

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Abstract. This paper presents the results of a study of meso-aryl-substituted porphyrin Langmuir monolayers by the method of compression isotherms. Experimental data were used to plot the dependences of the compression modulus ($C^1$) on the specific area. Monolayers at specific surface pressure were transferred to solid substrates and investigated. The monolayers were transferred to the surface of monocrystalline silicon at surface pressures of 8, 25, and 60 mN/m and examined them by atomic force microscopy (AFM) in a semi-contact mode. It was found that with an increase in the transfer pressure, the coarsening of molecular aggregates occurs. The smallest roughness is observed for a porphyrin film formed and transferred at a pressure of 8 mN/m.

1. Introduction
Thin films of porphyrin derivatives are a promising material for the creation of thin-film photosensitive and photovoltaic devices [1–3]. The properties of porphyrin strongly depend on the presence of peripheral substituents, the inclusion of metals inside the porphyrin ring, and various conformations [4]. All this gives designers great freedom to develop new devices with unique properties.

One of the important technological problems in obtaining multilayer structures is the formation of highly ordered monomolecular layers of porphyrin and their derivatives (PP) on solid substrates. Currently, there are many technologies for producing films and coatings, but it is the Langmuir-Blodgett (LB) technology that combines the possibility of forming monomolecular layers and the ease of implementation. Using the basic principle of LB technology (self-organization of substances at the water-air interface), it is possible to form PP monolayers with different packing densities and molecular orientations in the layer. Using the Langmuir-Schaeffer (LS) transfer technique, such layers are easily transferred to solid substrates, while the crystal structure of the monolayer that is formed on the surface of the water can be preserved on the solid substrate.

To obtain highly oriented defect-free Langmuir monolayers and LB films, it is important to understand the regularities of their self-organization at the air-water interface, which is a template that initiates both the 2D format and the orientation of molecules in the layer. The strict control of
technological conditions is important, in particular the amount of substance that is applied to the surface of the water.

The molecule of the symmetrically substituted porphyrin under study has 4 hexadecyloxyphenyl substituents in the mesopositions of the macrocycle [5]. This substitution gives reason to expect that the amphiphilic properties of these molecules will be maximized. This will facilitate better ordering of molecules in the ML on the water surface and more successful technological transfer of it to solid substrates.

One of the non-contact methods for controlling the structure of LB films, with the help of which it is possible to determine the surface morphology and dimensions of the formed nanoobjects, is the method of atomic force microscopy. In the course of previous experiments, in which the effect of the amount of surfactant in a solution of quantum dots on the structure of the resulting films was studied by atomic force microscopy, it was shown that the removal of excess oleic acid leads to a more ordered and dense packing of quantum dots [6]. The AFM method allowed the authors of [7] to show that protonated porphyrins form J-aggregates at the gas-liquid and liquid-liquid interface, the optical properties of which depend on the degree of compression. In study [8], the LB method was used to form chiral mesoscopic structures of two tetraphenylporphyrin derivatives functionalized with a steroid group in each of the four meso-positions. AFM made it possible to reveal the formation of rod-like aggregates intertwined in such films. The AFM method showed the inclusion of copper nanoparticles stabilized by the surfactant sodium dodecyl sulfate leads to an increase in stability, an increase in the value of surface potential, and the relief of the film transferred to a solid substrate has a pronounced macrostructure in the form of relatively large objects with dimensions of 300-500 nm in plan and height up to 80 nm [9].

The aim of the work is: to obtain floating (Langmuir) monolayers based on symmetrically substituted porphyrin and to study the influence of the conditions of their formation and transfer (the amount of solution introduced to the surface of the water subphase, the degree of compression of monolayers) on the morphology of thin films transferred to a solid substrate by the Langmuir-Scheffer method.

2. Materials and methods
Monolayers of porphyrin derivatives were formed and examined with a KSV NIMA 2002 KN LB bath (medium size bath with a compression ratio of about 1:9). Deionized water with a resistivity of 18.2 MΩ cm, which was obtained on a Smart2Pure unit from ThermoScientific, was used as the aqueous subphase. The studies were carried out at a room temperature of 24 °C. A solution of meso-aryl-substituted porphyrin (PP) in chloroform with a concentration of 5×10⁻⁴ M was used to form a monolayer. This porphyrin derivative (the structural formula of which is shown in Figure 1) was synthesized according to the method described in [5].

![Figure 1. Structural formula of the meso-aryl-substituted porphyrin compound.](image)

Different volumes of porphyrin solution were placed on the water surface – 50, 100, and 150 μL. The time for complete evaporation of the solvent was 10 min for each case, after which the ML was
compressed by two barriers at a constant rate of 13 mm/min (symmetric compression mode). The surface tension during compression was measured with a Wilhelmy balance.

The monolayer was transferred onto a solid n-type monocrystalline silicon substrate coated with a natural oxide. Immediately before the transfer of ML, the silicon surface was treated with chloroform. After reaching a given pressure (at surface pressures of 8, 25, and 60 mN/m) and relaxation of the monolayer, it was transferred by the Langmuir-Schaeffer method - a horizontal lift. Before scanning, the samples were dried at room temperature.

Then, the surface relief of the samples was examined using a SOLVER NANO scanning probe microscope (AFM NT-MDT). Scanning was carried out in a semicontact mode, with probes of the HA-HRA/W2C series with a resonance frequency of 230 kHz and a radius of curvature of the tip not exceeding 35 nm, at a scan recording speed of 0.8 Hz and an operating point current of 2.5 nm.

The resulting images were processed using the software for visualization and data analysis Gwyddion version 2.58 [10].

3. Results and Discussions

Figure 2 shows the \( \pi-A \) compression isotherms of the meso-aryl-substituted porphyrin compound depending on the volume sprayed on the surface of the aqueous subphase.

Compression isotherms showed an implicit dependence on the volume of the solution deposited on the surface of the subphase. The maximum compression pressure was 66 mN/m.

The calculated specific area \( A \) per molecule immediately after spreading (before compression) of the porphyrin solution was about 5.3; 3.9; 2.6 nm\(^2\) for 50, 100 and 150 \( \mu L \), respectively. The tight packing state for 50 \( \mu L \) was not achieved. No collapse was observed for volumes of 100 and 150 \( \mu L \).

The choice of pressure for the transfer of a monolayer to solid substrates was chosen from the following considerations. Were selected 3 areas in the compression isotherm plot for 150 \( \mu L \). These areas correspond to different phase states of ML. For them, the area per molecule in a monolayer \( (A_0) \) was calculated, which was obtained by extrapolating the linear section to the \( A \)-axis (Figure 3, one such tangent to the middle section of the isotherm is shown as an example). For each of the selected regions, the modulus of compression, compressibility and area per molecule in a monolayer were calculated. Knowledge of these parameters makes it possible to determine the phase states of a monolayer, to analyze and correct the conditions for deposition of the formed films on solid substrates.

Together with the compression isotherm, a \( C^1-A \) dependence was plotted (the dependence of the compression modulus on the specific area). It is noteworthy that this dependence exhibits local
maxima in the range of values from 0.47 to 0.37 nm$^2$. This indicates that achieving closest packing of amphiphilic molecules or fragments of amphiphilic molecules, ML components. Upon further compression, a multilayer structure begins to form.

Table 1 shows the values of the parameters of PP monolayers, calculated from the experimental curves: pressure of close packing of molecules $\pi_{tr}$, area $A_0$, modulus of compression $C_1$ of a monolayer, compressibility $K_0$.

![Figure 3. $\pi$-$A$ isotherms of meso-aryl-substituted porphyrin compound (blue curve) and $C_1$-$A$ Compression modulus dependence (black curve). Red areas correspond to areas tight molecular packing.](image)

| $\pi_{tr}$, mN/m | $A_0$, nm$^2$ | $C_1$, mN/m | $K_0$, m/mN | $L$, nm | $h$, nm | $R_a$, nm |
|-----------------|--------------|-------------|-------------|--------|-------|---------|
| 8               | 0.76         | 44          | 0.022       | 100-150| 5-10  | 2.3     |
| 25              | 0.62         | 117         | 0.0085      | 200-300| 10-15 | 3.8     |
| 60              | 0.60         | 134         | 0.0074      | 300-500| 10-20 | 6.9     |

At pressures of about 8 mN/m, the ML state can be classified as liquid-expanded, at which the modulus of compression is not constant due to the changing conditions of intermolecular interactions. At higher pressures, the packing of molecules in the ML changes little and the mechanical properties remain practically constant. This is an indirect indication that in the pressure region of 25 mN/m the ML is in a stressed state, but at these stresses its structure is preserved. At a pressure of about 60 mN/m stresses in the ML begin to form 3D objects, such as multi-layer folds of molecular aggregates.

AFM studies also indicate such rearrangements in the ML. For AFM studies, the formed monolayers were transferred onto solid substrates of monocrystalline silicon at transfer pressures of 8, 25, and 60 mN/m. Figure 4 shows AFM images and elevation profiles of a meso-aryl-substituted porphyrin compound. The obtained images of the relief show that on the samples with deposited films, at different transfer pressures, noticeable differences are observed: the shape of the nanoobjects and the features of the relief change. Typical dimensions of nanoobjects were 100-150 nm in plan and up to 10 nm in height for films obtained at a pressure of 8 mN/m, and at flat dimensions of 450-500 nm and a height of up to 20 nm for films obtained at a pressure of 60 mN/m, that is, the height and lateral dimensions of the objects increased with increasing transfer pressure.
Statistical processing of AFM images also showed the expected coarsening of molecular aggregates and an increase in film roughness with an increase in the surface transfer pressure to 60 mN/m. The root-mean-square roughness $R_a$ of the surface of the samples obtained was 2.3; 3.8; 6.9 nm at transfer pressures of 8; 25; 60 mN/m, respectively, i.e. a film of porphyrin molecules formed at a pressure of 8 mN/m has the smallest roughness, which may be associated with a lower aggregation of molecules.

**Figure 4.** AFM image of *meso*-aryl-substituted porphyrin (left) and their profiles (right) at transfer pressures: (a) 8 mN/m, (b) 25 mN/m, (c) 60 mN/m.

### 4. Conclusion

Thus, Langmuir monolayers and Langmuir-Schaeffer films of a *meso*-aryl-substituted porphyrin compound were studied in this work. Compression isotherms showed an implicit dependence on the volume of the solution deposited on the surface of the subphase. The mechanical parameters of the monolayer were determined for different aliquots. By extrapolating the linear region to the axis, the most favorable regions of the close packing of molecules for further transfer to solid substrates were revealed. Analysis of AFM images showed the expected coarsening of molecular aggregates and an increase in film roughness with increasing surface transfer pressure. The smallest roughness is observed in the PP film formed and transferred at a surface pressure of 8 mN/m, which may be associated with a lower aggregation of molecules.

### Acknowledgments

The study supported by a grant of the Russian Science Foundation (project No. 21-73-20057) and Saratov State University
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