The Formation of arachidic acid Langmuir monolayers on the 
NiCl₂ solution

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Abstract. The article describes the features of the formation of arachidic acid Langmuir 
monolayers on a water or NiCl₂ solution subphase surface. Monolayers structure was 
investigated by analyzing the compression isotherms and Brewster angle microscopy methods. 
Films on the solid substrate (glass plates) were investigated by atomic force microscopy 
method for morphology. Film structure was studied as a function of the concentration of salt in 
subphase and exposure time. It is shown that the structure of films obtained by using NiCl₂ 
solution as subphase is not homogeneous and we can see some grains in thin films.

1 Introduction
Today, one of the most important tasks in nanotechnology is the production of composite materials 
with predetermined properties. In particular, in micro and nanoelectronics, there is a problem of 
obtaining active and conducting layers (electrodes) in one process. Therefore, various methods aimed 
at obtaining composite thin films are actively developed and improved [1].One of the solutions to the 
above problem is the inclusion in the composition of organic films of various inorganic objects, 
nanoparticles [2], carbon nanotubes [3], graphene [4], etc. 
The Langmuir-Blodgett method is the simplest method that allows to obtain ordered layers of 
nanoobjects, using the principle of self-organization of objects on the interface of phases. This method 
is cheap, and also does not require special conditions (vacuum, elevated temperatures, etc.) for 
obtaining thin-film coatings. 

In our work we obtained Langmuir monolayers of arachidic acid using a different subphase. In the first stage (to obtain reference data) deionized water was used as a subphase. In the next stage (for the addition of metal ions to the subphase), the NiCl₂ solution with different concentration was used as a subphase. Researchers from Khomutov group [5] have previously found that metal ions from the subphase can react with surfactant molecules. And under specified conditions, this salt formation reaction leads to the formation of metallic nanoparticles under the monolayer (in the course of its 
compaction when the barriers are compressed) [6]. Nickel and lead salts are the most popular materials
for the formation of such type nanoparticles. In our work, we used nickel salt as less toxic (relative to lead).

2 Materials and methods
In all experiments we use deionized water (R about 18Mom×cm) as a subphase basis. For the addition of metal ions to the subphase we prepare NiCl$_2$ (Sigma Aldrich) solution in deionized water with concentration $10^{-3}$ and $10^{-2}$ M. To change the acidity of the solution a $10^{-2}$ solution of NaOH was used. Solution of arachidic acid (Sigma-Aldrich) prepared in chloroform (Vecton, Russia) with concentration $10^{-3}$ M.

For formation and deposition of monolayers we used KSV Nima LB trough KN 1003 (KSV Nima, Finland). Exposure time (it is time between the injection of the surfactant and the beginning of the compression) was different in few series of experiments: 5, 20, 40 minutes. For measure structure of monolayers we used Brewster angle microscopy method with Accurion NanoFilm Ultrabam microscope (field of view is 800*430 µm). Atomic force microscopy (AFM) picture taken in semicontact mode by Nanoeducator II AFM microscope.

3 Results and discussion
In the first series of experiments, we obtained monolayers compression isotherms for arachidic acid on the surface of pure deionized water and surface of NiCl$_2$ $10^{-3}$ solution by different exposure time (figure 1).

![Figure 1. Compression isotherms for arachidic acid monolayers on NiCl$_2$ solution by different time of exposure monolayers (arh standart – arachidic acid compression isotherm on pure deionized water surface)](image)

How we can see in this isotherms, they are shifted to the right. This region corresponds to a larger area per molecule of the monolayer. Since in all series of experiments the same arachid acid solution was used in the same concentration, this corresponds to an increase in the structural unit size in monolayer. In this case, this behavior of the monolayer can be explained by the course of the salt-formation reaction between surfactant and the metal ions from the subphase. In addition, monolayers also change their mechanical characteristics. In particular, the pressure of the phase transition between the phase states of the monolayer (fracture point at 27 mN/m for a monolayer of arachic acid on pure water) drops by 12%. The magnitude of the change is independent of the exposure time of the monolayer. In addition to the pressure of the phase transition, the collapse pressure of the monolayer also decrease. All these changes indicate serious structural rearrangements in the monolayer (under the conditions described above).
Therefore, in the second stage, the Brewster angle microscopy method was used to study monolayers directly in the process of formation. Figure 2 shows images of a monolayer for various composition of subphase by the same surface pressure value.

![Figure 2. Brewster angle microscopy pictures of arachidic acid monolayers for different compositions of the subphase (A – on pure water subphase, B – on 10^{-3}M NiCl\textsubscript{2} solution) by same value of surface pressure (about 10 mN/m).](image)

We can see in these images approximately the same nature of the structure of monolayers – the presence of a large number of clusters with identically oriented surfactant molecules (in this case, a different color indicates different optical properties of the sections of the monolayer, which in this case can be caused only by differences in the orientation of the molecules). However, in the presence of nickel ions in the subphase, the size of the clusters themselves is much smaller. And we did not find the dependence of their size on the exposure time of the monolayer. The effect of changing the size of clusters can be explained by the change in mechanical characteristics. Since the ratio "number of molecules at the cluster boundary / number of molecules in the cluster volume" gradually increases with decreasing size, all processes associated with lateral pressure occur at a lower value. Thus, the transmission of the impact to the cluster volume is faster (at lower values of the surface pressure of the monolayer).

To study the properties of films on solid substrates, they were transferred to glass plates. After that they were investigated by atomic force microscopy. Typical images are shown in Figure 3.

![Figure 3. AFM pictures for arachidic acid film on pure water (A) and NiCl\textsubscript{2} solution (B).](image)
The deposition of both films was carried out under the same conditions (surface pressure) by the Langmuir-Schaefer method. We applied a single monolayer. In these images we can see sections of a monolayer film. In figure 3A, such a part is located above the center of the image, and also characteristic circular discontinuities that are formed when the film dries out. The rest of the film is fairly homogeneous, and it does not have any grains or inclusions. In contrast, the film depicted in Figure 3B shows within itself certain grains or their conglomerates. In this case, their appearance is explained by the presence in the film of nanoparticles of nickel or their clusters, which give the film an inhomogeneous structure.

Conclusion

Thus, the results of the study showed that at a certain ratio between the composition of the subphase and the exposure time of the monolayer, it is possible to achieve the formation of metallic nanoparticles under the monolayer. We also established by microscopy of the Brewster angle the changes in the clustering of the monolayer upon addition of metal ions to the subphase. These changes provoke changes in the mechanical characteristics of the monolayer. The AFM method shows the structural differences in arachidic acid films obtained on pure water and NiCl₂ solution.

Acknowledgments

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