Formation of Gibbs and Langmuir floating layers based on copper nanoparticles: temperature and concentration effects

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Abstract. This paper is devoted to study of the formation of Gibbs floating layers from aqueous solutions of copper nanoparticles (Cu NPs) stabilized by the sodium dodecyl sulfate surfactant. Langmuir floating layers of arachidic acid formed on the surface of a water subphase containing Cu NPs were also studied. Adsorption of copper nanoparticles on a monolayer of arachidic acid at different conditions has been investigated. In the experiments the amount of copper nanoparticles in the subphase and the temperature of the subphase were changed. The performed analysis showed that the increase of subphase temperature from 29 to 42 °C leads to the increase of the area occupied by Langmuir floating layers in a liquid-condensed state by 30 and 32 %, respectively. After a single transfer of the floating layer onto the highly oriented pyrolytic graphite substrates, their surface microrelief was investigated by atomic force microscopy (AFM). The AFM scans showed that the obtained copper nanoparticles films contained separate areas with copper particles and their aggregates. With an increase of surface pressure from 10 to 40 mN/m, an increase of the height difference of the surface microrelief from 4 to 7 nm and an increase of the large aggregates number with lateral dimensions about 100 nm were observed.

1. Introduction

Recently, the number of publications devoted to the study of nanoparticles (NPs) properties, methods for modifying their surface, the formation of 2D systems on their basis at different interfaces has been grown steadily. One of the most common methods of formation such layers is Langmuir-Blodgett (LB) technology [1-3]. This method is simple in execution because it does not require the creation of specific technological conditions (high vacuum, use of complex equipment, etc.). The LB technology allows to create nanomaterials, control their composition, structure and properties by changing temperature, acidity, composition of subphase, etc. Moreover, it is possible consistently transfer formed floating layers of various substances to substrates [2-7]. In addition, this technology allows obtaining heterostructures with unique composition, structure and properties, which can be varied during the transition from layer to layer. Such films have potential application as electrodes in micro- and nanoelectronics devices (in photovoltaics, supercapacitors, etc.) [8, 9].

It is known that of soluble compounds Gibbs floating layers can be formed on the surface of water subphase, while Langmuir floating layers can be obtained of insoluble compounds. In both cases, the formation of floating layers is determined by many technological parameters such as ionic...
composition of subphase, its acidity, temperature, electrical and magnetic fields, radiation, surfactant’s nature and layer composition. Formation of NPs floating layers in an organic matrix is even more difficult technological process. Properties of NPs themselves as well as properties of surfactant shells stabilizing NPs are added to the influence of the above mentioned parameters.

Earlier studies showed that subphase temperature affects phase states of floating layer on compression isotherms. In number of articles it was noted that temperature increase can lead to disruption of ordering of surfactant molecules in floating layer: the areas of isotherms that at low temperatures corresponded to a liquid-condensed state at higher temperatures transformed into the areas characteristic of liquid-expanded state. However, for more complex systems such as floating layer of NPs, the temperature increase in a certain range results in greater ordering [4]. For such complex quasi-2D systems based on NPs, polymer molecules, molecular clusters, etc. the temperature increase can change the composition of floating layer and NPs shells due to increase of surfactant solubility, polymer rearrangement at the expense of weak bonds breaking and so on. In turn, all above mentioned can change macrostructure, physical properties and macroparameters of the layer. Under the action of temperature, the properties of the subphase itself change. For example, the diffusion rate of molecules and ions through laminar and turbulent layers of the subphase adjacent to the surface changes, which in turn affects the stability of the surfactant floating layer. We can speak of a general change in the properties of the whole subphase under the influence of temperature, if the diffusion, laminar and turbulent layers are comparable with the depth of Langmuir trough.

The structure of films deposited onto solid substrates can repeat the structure of floating layer. The transfer success depends on the nature and composition of studied substance, acidity and temperature of subphase, size of nanoinclusions in the organic matrix, condensation degree of floating layer, temperature of subsequent processing, oxidation degree of film components, etc. [5, 6]. The structure and composition of forming film can be varied by changing the condensation degree of floating layer and the formation of desired phase state, determined from compression isotherms, as well as from the "compressibility (or compression modulus) vs area per molecule" dependencies [2, 7].

As it was noted in [1, 2, 10-12], constant exchange processes take place between floating layer and liquid subphase, therefore the "layer – subphase" system is in thermodynamic equilibrium. Previously, we studied the dynamics of Langmuir layers of semiconductor NPs in various organic matrices of water-insoluble surfactants [4, 7, 13-15]. The studied surfactants demonstrated a relationship between sorption processes of NPs from solution to a Langmuir layer and the packing of NPs in the layer as well as layer's mechanical properties and its formation conditions.

Controlling the composition and structure of the NPs floating layer during its formation and transfer from the water surface to the surface of a solid substrate is more complex problem than in the case of monolayers (MLs) of one-component surfactants or mixtures of simple compounds. The questions of interaction and aggregation of NPs in quasi-2D systems, changes of their distribution and phase separation in floating layers of complex composition, solubility and stability of NPs layers during formation, structure and composition preservation during transfer onto solid substrates are not well understood.

The aim of this work is to study the floating layers formed by copper nanoparticles (Cu NPs) in an organic matrix at the "gas – liquid" interface using the compression isotherm method and surface microlrelief investigation/analysis of the Cu NPs films transferred onto solid substrates by atomic force microscopy (AFM).

2. Experimental

In this work, the source of NPs for the formation of floating layers was the water subphase. This subphase was a solution of NPs. A detailed description of the synthesis technique and the particle size distribution study of the obtained NPs are given in [16]. The developed method is based on the chemical reduction of copper ammonia in the aqueous solution of anionic surfactant, sodium dodecyl sulfate (SDS). For this study the molar ratio of salt (copper chloride) and reducing agent (hydrazine
hydrate) was 1:150 at \( \text{pH} = 11.2 \) of the reaction medium. A synthesis time was one hour, which allows to obtain Cu NPs with sizes in the range of 10-140 nm.

At the first, Gibbs floating layers of Cu NPs were formed by sorption of the NPs from the subphase volume to the "gas – liquid" interface. Then, we compared this process with the sorption of the NPs on the ordered Langmuir ML of arachidic acid (AA), which plays the role of a sorbent surface.

To obtain the subphase with required concentration of NPs, the deionized water with a specific resistivity of 18 M\( \Omega \times \text{cm} \) was used (it was prepared by the Thermo Scientific Barnstead Smart2Pure water treatment system, USA).

All studies were carried out in the Langmuir trough KSV Nima LB Trough Medium KN 2002 (KSV Nima, Finland). Water circulation thermostat LOIP LT-105 (Russia) was used for the thermostating of the subphase in the trough. The accuracy of temperature control and maintenance was one degree. Surface tension was measured by Wilhelmy plate method with an accuracy of 0.1 mN/m.

At the first step, the dependence of the floating layer properties on the number of NPs in the subphase volume was studied. In this case the temperature of water subphase was maintained constant and equal to 21 °C. Various aliquots of the synthesized Cu NPs (100, 200, 300, 400 and 500 \( \mu \)l) were added to 130 ml of deionized water directly in the LB-trough and mixed there with a glass rod. Then we waited 5 minutes to reach thermodynamic equilibrium between the surface and the volume of the subphase (the time required for the adsorption of Cu particles to the water surface from the volume). Then the surface area was symmetrically compressed by two moving barriers at a speed of 15 mm/min. At the same time, the recording of the dependence of the surface pressure on the area occupied by a layer of particles was obtained.

In the second step, the specificity of the formation of Cu NPs layer at different temperatures of water subphase and fixed number of NPs (for added aliquot equal 500 \( \mu \)l) was studied. The temperature of the water subphase at this step was 21, 29, 35 and 42 °C. The time intervals of the Gibbs layers formation, starting moments of the barriers movement and the data recording were the same as in the first step.

In the third step, the sorption of Cu NPs on the Langmuir ML of AA was studied. For this purpose, 50 \( \mu \)l of AA solution (Sigma-Aldrich) in chloroform (Vekton, Russia) with concentration of 10\(^{-3}\) M was spread on the surface of the water subphase with the addition of 500 \( \mu \)l of Cu NPs solution. The subphase temperature was 21 and 42 °C. The compression conditions were the same as at the formation of Gibbs floating layers.

Finally, on the fourth step of this work, thin films on the surface of solid substrates of highly oriented pyrolytic graphite (HOPG) were formed by a single transfer of the floating layer of Cu/AA using the Langmuir-Schaefer method with surface pressures of 10, 20 and 40 mN/m. The surface microrelief of the obtained films was investigated by AFM method in the semicontact mode with the help of Solver Nano scanning probe microscope (NT MDT, Russia).

3. **Results and discussion**

The compression (a) and expansion (b) isotherms of the Gibbs floating layers were obtained for different Cu NPs number in the subphase (Figure 1). It is the first step of the study performed in order to establish the dependence of mechanical properties of layers on NPs number. The increase of the amount of added Cu NPs solution into water subphase (for aliquots from 100 to 300 \( \mu \)l) leads to the increase of the surface pressure at the end of the compression process – from 0 to 9.4 mN/m. This indicates the active emergence process of the surfactant molecules and Cu NPs covered by surfactant shell to the "gas – liquid" interface at the allotted time of 5 minutes and evidences about increase of their number at the surface proportionally to their amount in volume. However, this amount of surfactant molecules is not yet sufficient to form close-packed layer. Therefore there is no inflection point on the compression isotherms. According to [1], this state of the surfactant layer can be interpreted as gaseous or liquid-expanded where the molecules practically do not interact with each other.
An increase of the Cu NPs number in the subphase volume (when the addition of the nanoparticle solution is 400 or 500 μl) leads to the appearance of an inflection point (Figure 1). In this case the close-packed state of the surfactant molecules in the layer is reached.

Figure 2 shows influence of the subphase temperature on the process Cu NPs sorption on the liquid surface during compression (a) and expansion (b) of a layer. At room temperature an inflection point is present on the compression isotherm. However, the state of collapse is not achieved. When the temperature of the subphase rises to 42 °C, the isotherms have signs of collapse (Figure 2, a). At the same time, the isotherms are shifted towards large areas. This indicates the increase of the surface concentration of the surfactant molecules and Cu NPs wrapped by the surfactant shell (Figure 3). Expansion isotherms (Figure 2, b) has less noticeable differences. This may be due to the manifestation of a stronger interaction and aggregation of Cu NPs located on the surface.

It should be noted that the sorption on the surface of the liquid subphase is more pronounced when there is a floating layer of AA. A shift of compression isotherms towards large areas is also present. The increase of the subphase temperature from 29 to 42 °C leads to an increase of the area occupied by Langmuir floating layers in a liquid-condensed state by 30 and 32 %, respectively (Figure 4).

This behavior can have many reasons, in particular, that the solubility of AA is lower than the solubility of SDS by several orders of magnitude, and the surface concentration of AA molecules is less dependent on temperature than the surface concentration of SDS molecules.

Figure 1. Compression (a) and expansion (b) isotherms obtained by adding different aliquots of Cu NPs solution to the subphase at 21 °C.

Figure 2. Compression (a) and expansion (b) isotherms obtained at different temperatures of the subphase with the addition of 500 μl of Cu NPs solution.
Another possible reason may be the partial substitution of SDS molecules for AA molecules in the shells of Cu NPs and this fact also increases the sorption interaction of Cu NPs with the AA molecules on the subphase surface.

A tendency to aggregation of Cu NPs sorbed to AA ML at temperature of water subphase 42 °C is also confirmed by the fourth step of this investigation, when the surface morphology of thin films was studied by AFM. These film were obtained by transfer of the floating layers onto the surface of HOPG substrates at different pressures of 10, 20 and 40 mN/m. It can be seen (Figure 5), when the transfer pressure increases, the number and size of the aggregates also increase. The film contains aggregates of Cu NPs about 100 nm and the height difference increases almost twice (from 4 to 7 nm).

Figure 3. Combined compression (curves 1 and 3) and expansion (curves 2 and 4) of Gibbs floating layers obtained by adding 500 μl of Cu NPs solution.

Figure 4. The compression isotherms of the Langmuir layers of AA on the surface of pure deionized water (curves 1 and 2) and on the Cu NPs subphase (curves 3 and 4).

Figure 5. AFM images of surface microrelief (a, b, c) and height profiles (d, e, f) of Cu NPs/AA films on HOPG substrates obtained at surface pressures: 10 (a, d), 20 (b, e) and 40 mN/m (c, f).
4. Conclusion
The Gibbs floating layers formed by the adsorption of copper nanoparticles stabilized by SDS amphiphile shell from the subphase volume to the "liquid – gas" interface as well as the Langmuir floating layers of arachidic acid formed on this interface were investigated by the method of compression isotherms.

It was shown that an increase of the number of Cu NPs in the subphase volume leads to an increase of both the number of water-soluble SDS molecules and the number of Cu NPs in the Gibbs floating layer. The close-packed state is reached when 400 or 500 μl solutions of Cu NPs were added to the subphase.

The increase of the subphase temperature intensifies the process of sorption of Cu NPs from the volume onto the subphase surface. The area occupied by the floating layer increases in both cases of formation of Gibbs floating layer of Cu NPs and Langmuir floating layer of arachidic acid.

AFM studies of thin films transfer red onto a solid substrate have shown that the degree of condensation of the floating layer significantly affects the degree of aggregation of Cu NPs. Number of aggregates, their lateral dimensions and height increase with increasing transfer pressure.

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