Journal of Advanced Materials and Technologies. 2025. Vol. 10, No. 1

Original papers
Nanostructured, nanoscale materials and nanodevices

УДК 538.9+537.9+537.31 DOI: 10.17277/jamt-2025-10-01-008-018

Formation of conductive layers based on carbon nanotubes by the Langmuir method

© Oday A. H. Hassoon[a,b]✉, Odai N. Salman[c], Tatiana Ya. Karatyshova[a], Ammar J. K. Al-Alwani[a,d], Maxim V. Gavrikov[a], Vladislav N. Mironyuk[a], Andrey M. Zakharevich[a], Mikhail V. Pozharov[a], Evgeny G. Glukhovskoy[a]

[a] *Saratov State University, 83, Astrakhanskaya St., Saratov, 410012, Russian Federation,*
[b] *Ministry of Electricity, Baghdad, P.O. Box 5815, Iraq,*
[c] *University of Technology, Baghdad, P.O. Box 19006, Iraq,*
[d] *Al-Furat Al-Awsat Technical University, Technical Institute Kufa, Kufa, Najaf Al-Ashraf, P.O. Box 54001, Iraq*

✉ uday_m82@yahoo.com

Abstract: The compression isotherm and potential jump methods were used to study Langmuir monolayers formed from individual solutions of carbon nanotubes (CNTs) and their mixtures with arachidic acid (AA) in various ratios. The optimal amount of CNT solution (200 μL) for forming a Langmuir layer was empirically found. When transferred to a solid substrate, the layer has an average conductivity of about $4.3 \cdot 10^{-12}$ S·sq^{-1}. It was also found that when applying the second and subsequent layers, the film conductivity increases by more than 6 orders of magnitude (up to $5.08 \cdot 10^{-6}$ S·sq^{-1}). In the study of mixtures of carbon nanotube solutions (without amphiphilic properties) and arachidic acid (a typical representative of a surfactant), an optimal ratio of the volumes of the prepared solutions was found (CNT : AA – 80 : 20), at which it is possible to control the degree of compression of the carbon nanotube layer on the surface of the aqueous subphase. It was shown that the introduction of AA molecules into the composition of CNTs allows an additional increase in the films conductivity by more than two orders of magnitude (up to $1.18 \cdot 10^{-3}$ S·sq^{-1}), compared to films of individual CNTs. The studied films can be used as a platform for the creation of various devices for micro- and nanoelectronics, optoelectronics, photovoltaics and flexible electronics.

Keywords: Langmuir-Blodgett method; carbon nanotubes; Langmuir monolayers; arachidic acid; surface tension; thin films conductivity.

For citation: Hassoon OAH, Salman ON, Karatyshova TYa, Al-Alwani AJ, Gavrikov MV, Mironyuk VN, Zakharevich AM, Pozharov MV, Glukhovskoy EG. Formation of conductive layers based on carbon nanotubes by the Langmuir method. *Journal of Advanced Materials and Technologies*. 2025;10(1):008-018. DOI: 10.17277/jamt-2025-10-01-008-018

Формирование проводящих слоев на основе углеродных нанотрубок методом Ленгмюра

© О. А. Х. Хассун[a,b]✉, О. Н. Салман[c], Т. Я. Каратышова[a], А. Ж. К. Аль-Алвани[a,d], М. В. Гавриков[a], В. Н. Миронюк[a], А. М. Захаревич[a], М. В. Пожаров[a], Е. Г. Глуховской[a]

[a] *Саратовский национальный исследовательский государственный университет имени Н. Г. Чернышевского, ул. Астраханская, 83, Саратов, 410012, Российская Федерация,*
[b] *Министерство электроэнергетики, Багдад, 5815, Ирак,*
[c] *Технологический университет, Багдад, 19006, Ирак,*
[d] *Аль-Фурат Аль-Авсат Технический университет, Технический институт Куфа, Куфа, Наджаф, Аль-Ашраф, 54001, Ирак*

✉ uday_m82@yahoo.com

Аннотация: Методом изотерм сжатия и методом скачка потенциала исследованы ленгмюровские монослои, сформированные на основе индивидуальных растворов углеродных нанотрубок (УНТ) и их смесей с арахиновой кислотой (АК) в различных соотношениях. Эмпирически найдено оптимальное количество раствора УНТ

(200 мкл) для формирования ленгмюровского слоя, который при переносе на твердую подложку имеет среднюю проводимость около $4.3 \cdot 10^{-12}$ См/кв. Обнаружено также, что при нанесении второго и последующих слоев проводимость пленки увеличивается более чем на 6 порядков (до $5{,}08 \cdot 10^{-6}$ См/кв). При исследовании смесей растворов углеродных нанотрубок (не имеющих амфифильных свойств) и арахиновой кислоты (типичного представителя поверхностно-активного вещества) найдено оптимальное соотношение объемов приготовленных растворов (УНТ : АК – 80 : 20), при котором возможен контроль степени сжатия слоя углеродных нанотрубок на поверхности жидкости. Показано, что введение в состав УНТ молекул АК позволяет дополнительно повысить проводимость пленки более чем на два порядка (до $1{,}18 \cdot 10^{-3}$ См/кв), по сравнению с пленками индивидуальных УНТ. Исследованные пленки могут быть использованы в качестве платформы для создания различных устройств микро- и наноэлектроники, оптоэлектроники, фотовольтаики, а также гибкой электроники.

Ключевые слова: метод Ленгмюра-Блоджетт; углеродные нанотрубки; ленгмюровские монослои; арахиновая кислота; поверхностное натяжение; проводимость тонких пленок.

Для цитирования: Hassoon OAH, Salman ON, Karatyshova TYa, Al-Alwani AJ, Gavrikov MV, Mironyuk VN, Zakharevich AM, Pozharov MV, Glukhovskoy EG. Formation of conductive layers based on carbon nanotubes by the Langmuir method. *Journal of Advanced Materials and Technologies*. 2025;10(1):008-018. DOI: 10.17277/jamt-2025-10-01-008-018

1. Introduction

Carbon nanotubes (CNTs) are interesting to experts in many scientific and applied fields, primarily due to their conductive properties [1]. For many years, they have been the focus of attention of developers of micro- and nanoelectronics devices (including flexible electronics), electrical energy storage devices, photovoltaic devices, etc. [2–4].

In the development of solar cells, ultra-high-capacity devices, photodiodes [5], photoconductors [6], bolometers [7] and other electronic devices, an important issue is obtaining a thin conductive coating. Carbon nanotubes are one of the materials that are well suited for solving this problem [8]. Thus, counter electrodes (CE) are made on the basis of CNTs in modern photovoltaic devices. The photoelectric characteristics, long-term stability of operation, and the cost of these devices depend significantly on their efficiency [9]. For this reason, the search for new materials and the development of optimal and inexpensive technological solutions remain relevant. Many methods are used to obtain film CE based on CNTs: vacuum deposition, chemical deposition from a solution, spin coating, etc.

Nanotubes can be divided into single-walled and multi-walled CNTs (SWCNTs and MWCNTs, respectively) according to their structural features. According to their electrical properties, semiconductor (s-SWCNTs) and metallic (m-SWCNTs) CNTs are distinguished among SWCNTs. At the same time, metallic properties are most typical for MWCNTs [10, 11]. MWCNTs have a fairly high work function of 4.8–5 eV, and electrical conductivity can reach values of the order of 10^6 S·m^{-1} [12].

In [13], a composite material based on MWCNTs with platinum nanoparticles on their surface for CE was proposed to increase the electrochemical activity and efficiency of the solar cell. The material was applied using the spin-coating method. The use of a fairly expensive initial component (platinum nanoparticles) and the application method (spin-coating) casts doubt on the prospects for mass production of such cells.

One of the simplest methods of film deposition in technical implementation is the Langmuir-Blodgett Technique (LB) [14]. To form a monomolecular Langmuir layer on the surface of water, a necessary condition is the presence of amphiphilic properties in the molecules that make up this layer [15, 16], such as in the molecules of fatty acids and their salts [17, 18], phospholipids [19, 20], liquid crystals [21–23], etc.

In addition to amphiphilicity, an important factor in the formation of a dense ordered Langmuir layer is the steric factor. In the case of the formation of a monolayer of large molecules with a complex structure, simpler molecules are often added to them, which not only fill the voids, but also increase the mechanical strength and stability of the layer [23, 24].

There are many studies on the formation of CNT films using the LB method. The works [25–28] describe that despite the fact that the authors were able to obtain ultra-thin films with high electrocatalytic capabilities, the conditions they chose for applying the films did not allow achieving high continuity and homogeneity of the coating: the resulting films exhibited a mesh structure and relatively large helicoidal CNT clusters in the layer composition. In this regard, the goal of this work was to develop a technology for obtaining CNT films with high conductivity and homogeneity.

2. Materials and Methods

2.1. Materials and solutions

Multilayer CNTs (CTI Materials, USA) were used to form CE films [29]. CNT characteristics: content of the main substance > 95 wt. %; diameter ≈ 30–50 nm; length ~ 1–50 μm; ash content < 1.5 wt. %. Arachidic acid (AA) (Fluka) with a content of the main component > 99% was used as an amphiphilic matrix.

To prepare the solutions, we used standard grade chloroform (Component-Reactive, Russia) with a main substance content of > 99.9 %. The same chloroform was used for the preliminary treatment of the substrates and the working area of the Langmuir bath. To form floating layers based on CNTs, two basic working solutions were prepared: individual CNTs in chloroform with a concentration of $C = 1.2\times10^{-3}$ g·mL^{-1} and individual arachidic acid (AA) in chloroform with a concentration of $C = 0.5\times10^{-3}$ M.

Based on these solutions, mixtures of CNT and AA solutions were prepared with the following volume ratios of basic solutions $V_{\mathrm{CNT}} : V_{\mathrm{AA}}$ – 100 : 0, 95 : 5, 90 : 10, 80 : 20, 70 : 30, 50 : 50, 30 : 70, 10 : 90, 0 : 100.

2.2. Preparation of working solution

The basic CNT solution was prepared in two stages. First, a 0.12 g sample of CNT was dissolved in 10 mL of chloroform. The suspension was homogenized using a Hielscher Ultrasonics UP200Ht probe-type ultrasonic homogenizer (Hielscher, Germany, maximum power – 200 W, operating frequency – 26 kHz) at a power of 140 W for 15 min. To reduce chloroform evaporation, the neck of the vial in which the solution was prepared was covered with a polyethylene membrane, it was pierced, and the homogenizer probe was inserted through the pierce. The resulting homogenized CNT suspension was diluted tenfold by adding 9 volumes of chloroform to 1 volume of the suspension. After dilution, the homogenization procedure was repeated, as indicated above. As a result, a homogeneous base solution with a CNT concentration of $C = 1.2\times10^{-3}$ g·mL^{-1} was prepared.

Homogenization was not required to prepare the basic working solution of the native AA. Arachidic acid dissolves well enough in chloroform to form a true solution.

Based on the obtained solutions, immediately before the monolayer studies, solutions of a mixture of CNTs and AA were prepared using the following volume ratios of the basic solutions $V_{\mathrm{CNT}} : V_{\mathrm{AA}}$ – 100 : 0, 95 : 5, 90 : 10, 80 : 20, 70 : 30, 50 : 50, 30 : 70, 10 : 90, 0 : 100. Before mixing, the basic solutions were additionally treated in a Sapphire ultrasonic bath (Russia, maximum power – 200 W) at a power of 140 W. After mixing, the vial with the finished mixture was also treated in an ultrasonic bath for 30 min.

The procedure of ultrasonic treatment of solutions in the Sapphire ultrasonic bath was also carried out during the preparation of mixtures of CNTs with AA and before each introduction of the solution onto the water surface.

2.3. Methods for the formation of Langmuir layers on the surface of water and films on solid substrates

The formation and transfer of Langmuir layers was carried out using a KSV NIMA 2002 KN LB bath (Biolin Scientific, Finland), a medium-sized bath with a compression ratio of about 1:9.

Distilled water was used as the liquid phase. The water temperature in all experiments was 24 °C and was controlled with an accuracy of 0.2 °C.

To form a Langmuir layer on the water surface, the studied solutions were added dropwise using a chromatographic microsyringe (USA, Hamilton Co.). After instillation, 7 min were allowed for complete evaporation of the solvent, and then the compression of the Langmuir layer began. The amount of solution added to the water surface was preliminarily calculated so that after the evaporation of the solvent before the start of compression, some free space remained between the molecules, and they did not interact with each other, i.e., the so-called true monolayer (TM) was formed.

Surface tension (pressure) π was measured by the Wilhelmy plate weighing method. The value of π was controlled by an electronic Wilhelmy balance with an accuracy of 0.03 mN·m^{-1}.

The Langmuir layer was compressed symmetrically by moving barriers; the speed of movement of the barriers during compression was constant and amounted to 25 mm·min^{-1}.

To obtain additional information on the processes of changing the orientation of molecules in the layer, the surface potential jump method was used – the dependence of the change in the surface potential *SPot* on the area (*S*) occupied by the Langmuir layer, or on the area per molecule (*A*). *SPot* was measured by a KSV NIMA SPOT surface potential sensor with an accuracy of 1 mV.

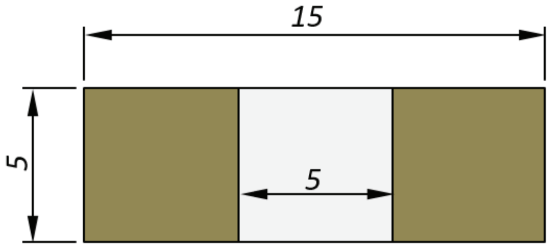


Fig. 1. Layout of the contact group on glass substrates

The transfer of layers from the water surface to the surfaces of solid substrates was carried out using the Langmuir-Schaeffer (LS) method – a variant of application when the substrate is oriented horizontally at the moment of contact with the Langmuir layer.

For the amphiphilic substance – arachidic acid, the Langmuir layer was transferred to a state of dense packing of molecules, i.e. at a surface pressure of $\pi = 20\ \mathrm{mN{\cdot}m^{-1}}$.

Glass plates with a conductive indium-tin oxide (ITO) film with a thickness of 120–160 nm and a specific surface resistance of 9–15 Ohm per square, manufactured by Luminescence Technology Corp. (Lumtec), Taiwan, were used as substrates. The size of the glass substrates was $15 \times 5\ \mathrm{mm^2}$. In the central part of the substrate, ITO was etched to obtain an area with a clean square glass surface (see the diagram in Fig. 1).

The presence of lateral contacts to the central region makes it possible to directly measure the value of the specific surface resistance of the studied Langmuir layers of CNTs applied to the central region.

2.4. Analytical methods

The surface morphology and film thickness on solid substrates were studied by scanning electron microscopy. For this purpose, we used a field emission scanning (raster) electron microscope FEI Inspect F50 (Spain), equipped with a Schottky source with field emission at a resolution of 0.8 nm in high vacuum mode at 30 kV, in combination with optimized geometry of the working chamber and a four-axis motorized eucentric sample tilt stage. We also used a field emission scanning electron microscope Mira II LMU (TESCAN, Czech Republic), equipped with an integrated elemental composition determination system AztecLive Advanced Ultim Max 40 and Inca Wave 500.

To study the conductive properties of the obtained films using the current-voltage characteristics (*I*–*V*) method, a stand for measuring electrophysical characteristics was used, consisting of an Agilent (Keysight) B1500A parameter analyzer and a PM-5 probe station. The module in the analyzer allowed precision measurements with a current resolution of 10 fA when applying a voltage of 100 V. The *I*–*V* characterisitcs were recorded with a voltage step of 0.5 V, the voltage sweep amplitude was 10 V.

3. Results and Discussion

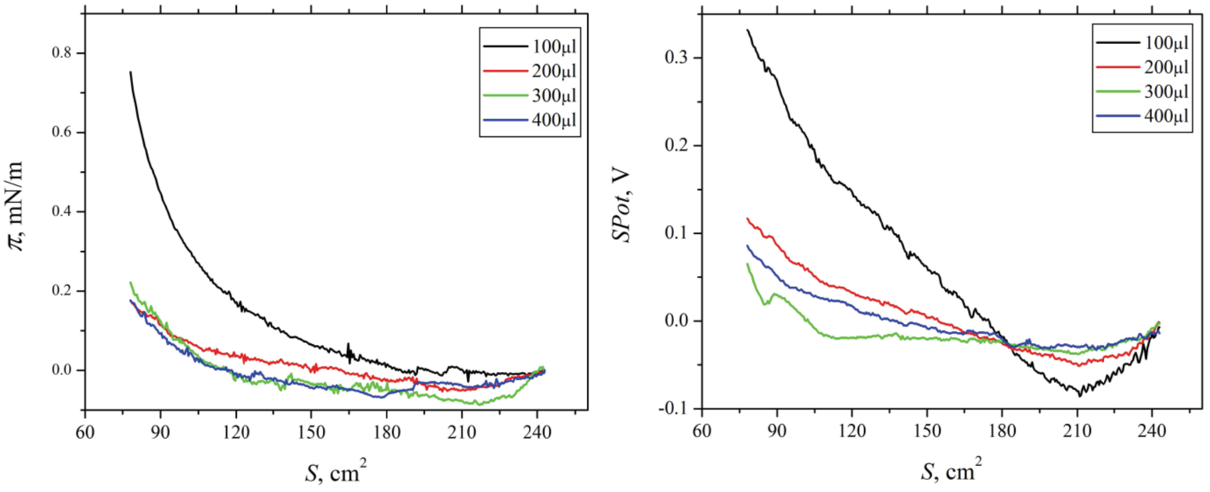
3.1. A study of Langmuir layers on the surface of water

At the first stage of the research, it was necessary to determine the optimal volume of CNTs for the formation of a Langmuir layer. In this case, optimization involved finding the conditions for obtaining the most homogeneous Langmuir layer (a Langmuir layer of CNTs close to the true one, if we use the terminology applied to amphiphilic substances) and, at the same time, a layer with good conductivity.

The following values of the volume of the working solution of CNTs introduced onto the surface of the aqueous phase were selected for the studies: $V_{\mathrm{CNT}} = 100$, 200, 300 and 400 μL. Despite the fact that CNTs are not amphiphilic substances, the type of compression isotherms depended quite strongly on V_{CNT} (Fig. 2).

It is easy to see that for $V_{\mathrm{CNT}} = 100$ μL the surface pressure reaches the highest values $\pi = 0.73\ \mathrm{mN{\cdot}m^{-1}}$ at the end of the layer compression. This may be due to the fact that at such a volume the surface concentration of CNTs is so small that there is some free area between them and their more optimal repacking occurs. Quite a strong variation in the surface potential during the compression of the CNT layer also indicates this. Of course, it is not possible to calculate the specific area in a close-packed state using the $\pi(A)$ and $SPot(A)$ dependencies, as is done in the case of classical surfactants. For the Langmuir layer of CNTs, it is necessary to take into account only indirect signs, such as the nature of the dependencies of the surface pressure and potential. It is the focus on them that makes it possible to achieve reproducibility of results or scaling of the technology.

At larger volumes of the working solution $V_{\mathrm{CNT}} = 300$ and 400 μL, the surface concentration of CNTs is so high that even when such quantities of working solutions are introduced onto the surface of the aqueous phase, the formation of a multilayer system occurs almost immediately, for which the surface pressure and surface potential change very slightly during compression of the layer.



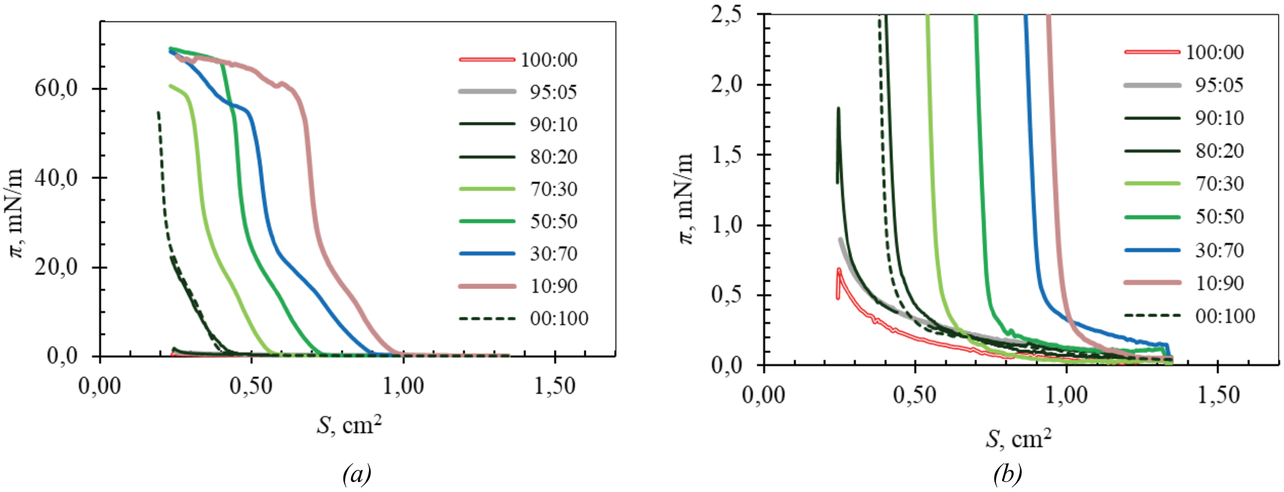
(a) *(b)*

Fig. 2. π–*S* (*a*) and *Spot*–*S* (*b*) dependencies for a CNT-based Langmuir layer formed using different volumes of working solution

Thus, from the selected amounts of working solution, the most compromise was the volume of working solution $V_{\text{CNT}} = 200$ μL. On the dependence *SPot*(*A*) one can observe the same type of curve with a clearly visible minimum, as in the case for $V_{\text{CNT}} = 100$ μL. As further studies showed, the same amount (200 μL) was the most acceptable for obtaining films with higher conductivity.

At the second stage, the effect of arachidic acid additives (a classic surfactant) on the properties of CNT Langmuir layers was investigated. The main motivation for adding a typical representative of the surfactant class to a non-amphiphilic substance was to obtain "feedback" on the degree of compression of the CNT Langmuir layer and the magnitude of the end pressure on this layer. As is known, monolayers of AA and their salts are well studied and often serve as model objects for which the dependences of crystalline and mechanical parameters on compression are known [30]. They are often used not only to clarify the concentrations of solutions or calibrate Langmuir baths. On their basis, diffraction gratings with a known, well-reproducible period of the crystal lattice are created, which are used in X-ray diffractometry [31].

The method of compression isotherms was used to study Langmuir layers of mixtures of basic working solutions of CNTs and AA with volume ratios $V_{\text{CNT}} : V_{\text{AA}}$ – 100 : 0, 95 : 5, 90 : 10, 80 : 20, 70 : 30, 50 : 50, 30:70, 10 : 90, 0 : 100. For each case, the volume of the mixture applied to the surface of the aqueous phase was the same and was 200 μL. The obtained π–*A* dependences are presented in Fig. 3.



(a) *(b)*

Fig. 3. π–*A* dependences for ML mixtures of CNTs and AA with different volume ratios of base working solutions: *a* – general view of compression isotherms; *b* – region of low surface pressures

As can be seen from Fig. 3, when compressing a monolayer of individual CNTs (curve 100 : 0 in Fig. 3), the maximum surface pressure barely reaches 0.8 $mN \cdot m^{-1}$ at the end of the layer compression, which once again confirms the absence of amphiphilic properties in carbon nanotubes. It can also be seen that the greater the proportion of AA contained in the mixture, the more the isotherm of the Langmuir layer became similar to the isotherm of the AA monolayer, which, in principle, is quite expected. For the isotherms of the monolayer of CNT : AA mixtures with ratios of 95 : 5, 90 : 10, 80 : 20, 70 : 30, 50 : 50, 30 : 70, 10 : 90, 0:100 in the π range from 0.5 $mN \cdot m^{-1}$ and below (below the so-called "breakaway point" of the isotherms, when the surface pressure begins to increase rapidly during the compression of the layer), the state of the monolayer is close to the states of the "two-dimensional gas" and "liquid-expanded" types (see Fig. 3*b*). A monolayer in such a state is characterized by a disordered orientation of the chains of AA molecules filling the free spaces between the CNTs. The parts of the π–A dependence curves above the "breakaway point" can be divided into two more sections: in the range of $\pi = 0.5 \div 20–25$ $mN \cdot m^{-1}$ and in the range of $\pi = 20–25 \div 55–60$ $mN \cdot m^{-1}$. In the first section, the surface pressure increases less intensively during layer compression than in the second, and it can be classified (using the classification of 2D phase states for a monolayer of fatty acids) as a *liquid condensed* state. Here, the AA molecules take a vertical position, but there is still no clear orientation of the hydrocarbon chains. The phase state of the Langmuir layer in the second section (with a steeper slope) can be attributed to the solid-crystalline state [15, 32], in which the hydrocarbon chains of the AA are tightly packed, well ordered, and a strict correlation is observed between the atoms of adjacent molecular chains. In the pressure region above 55–60 $mN \cdot m^{-1}$, large 3D objects begin to form in the monolayer of the mixture – multilayer folds that become visible to the naked eye; the collapse of the Langmuir layer occurs.

Based on the analysis of compression isotherms, the following conclusion can be made: in the case where the ratio of the volumes of the working solutions $V_{\mathrm{CNT}} : V_{\mathrm{AA}}$ is 80 : 20, the composition of the CNT : AA mixture layer contains a minimum amount of AA, which is quite sufficient to assess the degree of compression of this layer.

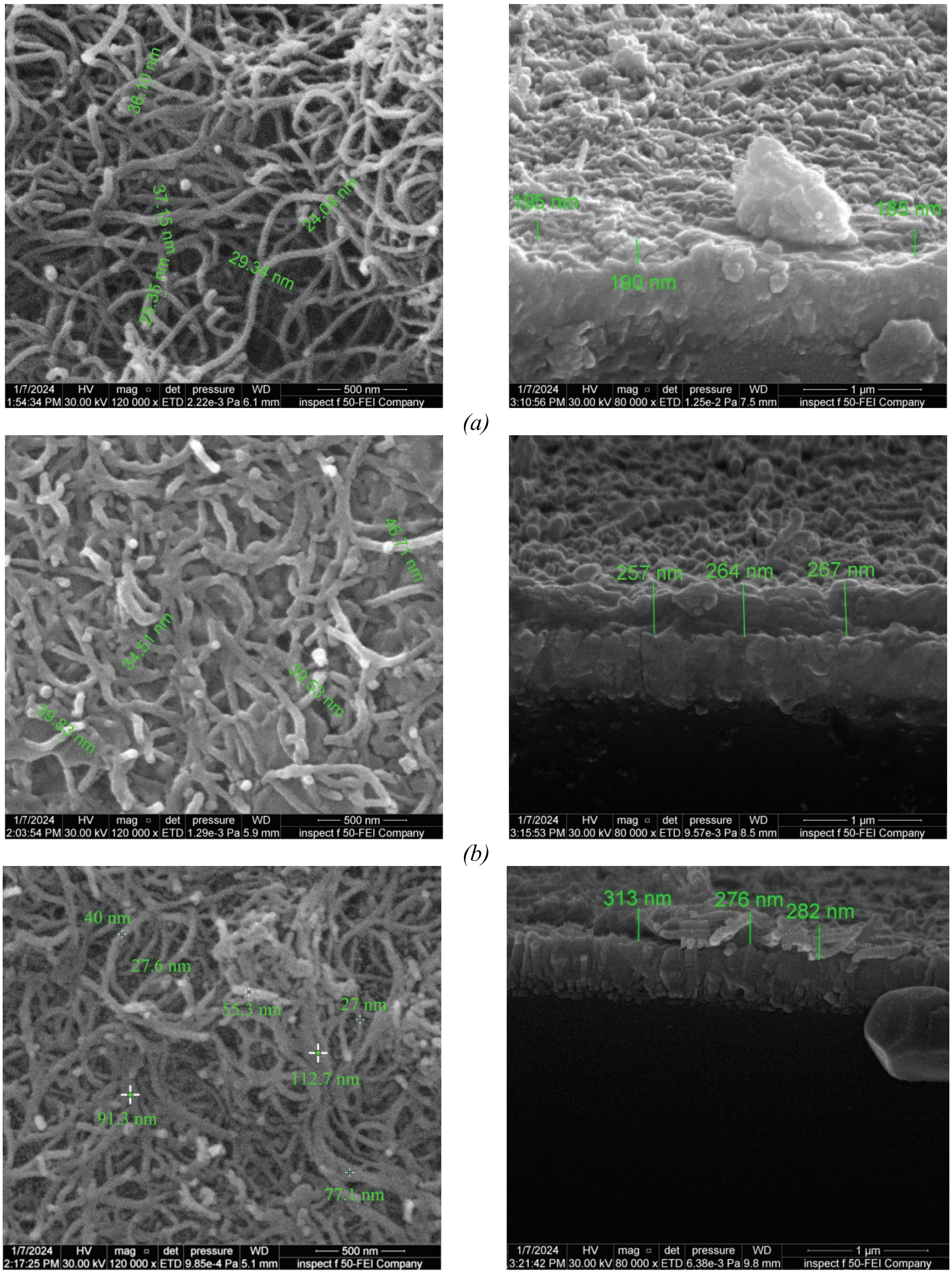
3.2. Preparation of films on solid substrates and study of their morphology

To transfer Langmuir films on a solid substrate, it was necessary to select the optimal value of surface pressure, which would be maintained by the bath automation at the time of transfer. The pressure at which the layer is restructured from a liquid-expanded to a solid-crystalline state was selected as such: 20–25 $mN \cdot m^{-1}$. At this pressure, the molecules in the layer already begin to pack into a 2D solid crystal, but mechanical stresses are still minimal. This combination of conditions should contribute to obtaining the most homogeneous film on the surface of the solid substrate. The film was deposited on the substrate immediately after reaching the specified surface pressure. The remaining conditions for the formation and compression of Langmuir layers were the same as in the studies. The efficiency of monolayer transfer to a solid substrate was estimated by the transfer coefficient $TR = \Delta A_l / A_s$ (*transfer ratio*, the ratio of the decrease in the monolayer area A_l during deposition to the substrate area A_s). In our case, very good transfer of each layer was observed – the value of the transfer coefficient was very close to 1, which indicates the high efficiency of the process.

To study the morphology, 3 types of LS films were prepared on a solid substrate (glass with ITO) with 5 layers each, which were formed using basic working solutions of CNTs in the amount of $V_{\mathrm{CNT}} = 100, 200, 300$ μL. FESEM microimages of the obtained samples (top view and cross-section) are shown in Fig. 4.

The CNT diameters were determined from the images, which basically confirm the passport data ($\varnothing = 30–50$ nm), although individual objects from 25 to 70–110 nm (for CNT aggregates) can be found in the images. The film thickness d, found from the cross-sectional views, depended on the used volume of the working solution V_{CNT} and changed in the series $d = 190, 263, 290$ nm for $V_{\mathrm{CNT}} = 100, 200, 300$ μL, respectively (Fig. 4).

The X-ray diffraction patterns for the obtained films were absolutely identical and contained a peak characteristic of CNTs, located at $2\theta = 26.1°$ (Fig. 5). The diagram shows a number of peaks corresponding to the presence of interatomic bonds of CNTs, as has been shown by other researchers [13, 33].



(a)

(b)

(c)

Fig. 4. FESEM image of nanotube film prepared using different volumes of CNTs:
a – 100 µL; *b* – 200 µL; *c* – 300 µL (left – top view; right – cross-section)

3.3. A study of conductive properties of films on solid substrates

To study the conductive properties, samples with three types of films were obtained from basic working solutions of individual CNTs, individual AA and a solution of a CNT:AA mixture with a volume ratio of 80:20. The layers were applied to glass substrates.

At the first stage, the dependences of the conductive properties of the films on the number of layers were studied. The obtained *I–V* characteristics for the number of layers from 1 to 7 are shown in Fig. 6*a*.

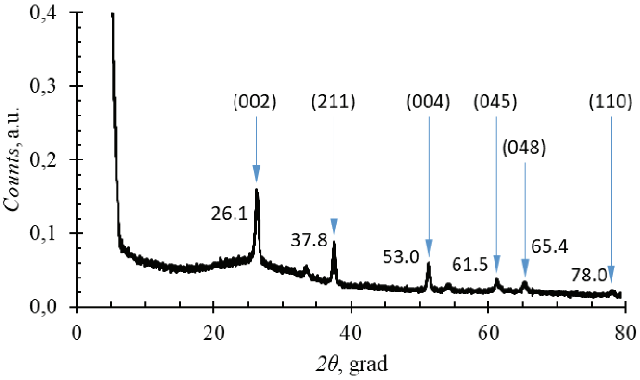


Fig. 5. Typical X-ray diffraction pattern of samples with LS CNT films

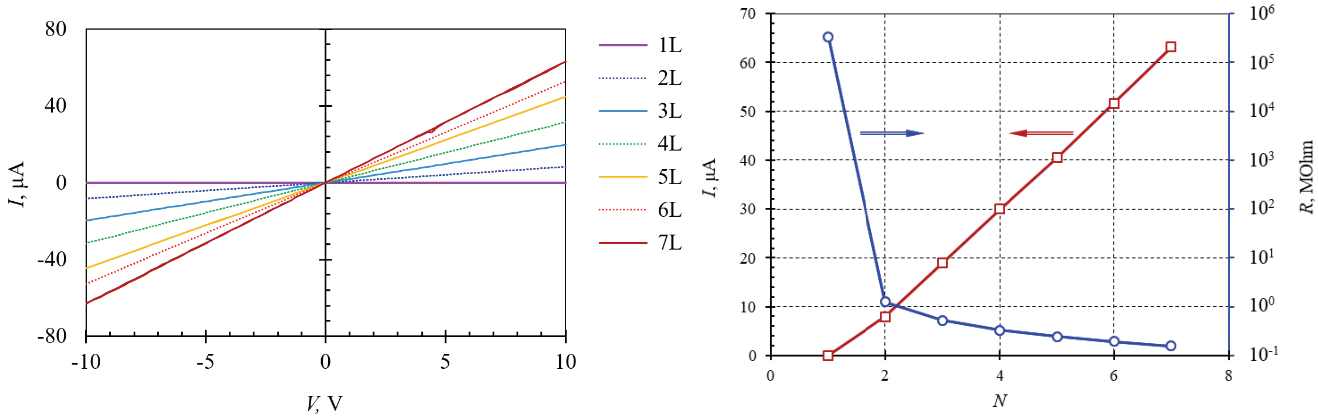
As can be seen from Fig. 6*b*, the values of maximum currents $I_{\max}$ for amplitude values of voltage $V = 10$ V increase linearly with the increase in the number of layers *N*. Such a dependence is quite logical if each layer, represented as a separate resistance, is "connected" in the equivalent circuit in parallel to the previously applied resistance layers. The same diagram (Fig. 6*b*) shows the dependence of resistance *R* on *N* in a semi-logarithmic scale.

When analyzing the dependence of the maximum currents $I_{\max}(V = 10\text{ V})$ on the number of layers *N*, the following interesting fact can be noted: the layer has an average conductivity of about $4.3 \cdot 10^{-12}$ S·sq^{-1}. This is significantly lower than the conductivity of the layers deposited on top of it, but, at the same time, more than an order of magnitude higher than the conductivity of the clean substrate. If we assume that the conductive properties of the first layer are the same as those of the other layers of the film, then, of course, the resulting linear graph of the dependence of $I_{\max}(V = 10\text{ V})$ on *N* will pass through the origin of coordinates while maintaining the general slope of the graph. However, the experimental dependence indicates that the conductive properties of the first layer differ radically from the conductive properties of the other layers. In this regard, it is quite logical to assume that even with high transfer efficiency (with a transfer coefficient value very close to unity), the first layer has many defects in its structure. The same can be observed during epitaxial growth of layers in heterostructures. Thus, the first layer of CNT serves as a kind of transition layer from the structure of the substrate to the structure of the next layer. When the second layer is applied, defects (such as voids) are "healed", as a result of which the current flow is restored.

At the next stage, the effect of adding arachidic acid on the conductive properties of the films was investigated. Three types of films were prepared by fivefold transfer of Langmuir layers from the surface of water of different compositions: formed from the basic working solution of individual CNTs, from the basic working solution of individual AA, and formed from a mixture of CNTs and AA with a volume ratio of the basic working solutions of 80 : 20, respectively. The deposition occurred on glass substrates with an ITO electrode system (see Fig. 1).

The *I–V* characteristics obtained in this study are shown in Fig. 7 – for ease of comparison of the obtained curves, the data are presented in a semi-logarithmic scale and the current values are taken modulo.

It can be seen that the AA film exhibits typical dielectric properties with typical current values $I_{AA} = 22 \div 28 \cdot 10^{-12}$ A with a voltage sweep of up to $V = -10 \div 10$ V (i.e. the average conductivity of the sheet was $G_{sh} = 2.53 \cdot 10^{-12}$ S·sq^{-1}). In addition, for AA, as for many dielectric materials, the presence of



(a) *(b)*

Fig. 6. Dependence conductive properties of the CNT films on the number of layers *N*:
a – current-voltage characteristics; *b* – values of current $I_{\max}$ and resistance *R* at voltage $V = 10$ V

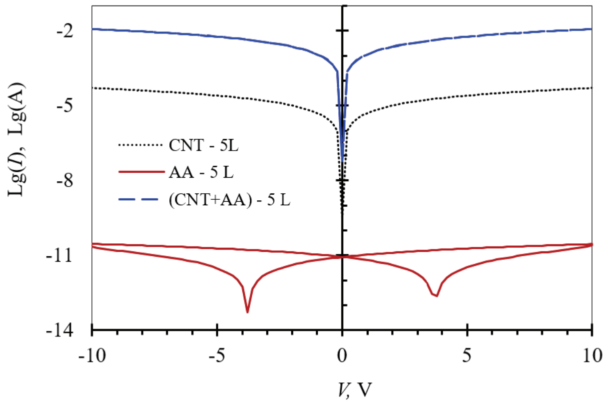


Fig.7. The *I–V* characteristics of different compositions films

polarization effects is characteristic, which is manifested in the presence of hysteresis on the current-voltage characteristics.

Current levels for the CNT film are approximately 6 orders of magnitude higher than those of the AA films, which was also expected. $I_{\text{CNT}} = 50.9 \div 50.8 \cdot 10^{-6}$ A with a voltage sweep of up to $V = -10 \div 10$ V (i.e. the average conductivity of the sheet was $G_{sh} = 5.08 \cdot 10^{-6}$ S·sq^{-1}). There are no hysteresis phenomena on their current-voltage characteristics. The dependence of the current on the voltage is almost linear and can be described by the ohmic law.

The conductivity of the films obtained from a mixture of CNT solutions with the addition of arachidic acid turned out to be more than 2 orders of magnitude higher than the conductivity of individual CNT films. $I_{AC} = 11.8 \div 11.8 \cdot 10^{-3}$ A with a voltage sweep of up to $V = -10 \div 10$ V. A peculiar synergetic effect was manifested for such a mixture, as a result of which the conductivity of CNTs with the addition of a dielectric material became significantly higher. The average values of sheet conductance and sheet resistance were $G_{sh} = 1.18 \cdot 10^{-3}$ S·sq^{-1} and $R_{sh} = 847$ Ohm·sq^{-1}, respectively.

Of course, clarifying the physical nature of the observed effect requires additional structural studies, but one of the reasons for the increase in current for the CNT : AA system may be a higher ordering and packing density of CNTs when arachidic acid molecules are embedded in the free spaces between individual CNTs.

4. Conclusion

Thus, the paper investigated Langmuir layers based on solutions of individual carbon nanotubes and mixtures of CNTs with arachidic acid, which were formed on the surface of water. For layers of individual carbon nanotubes, the effect of the amount of the working solution (100, 200, 300 and 400 μL) applied to the surface of water to form a monolayer on the compression isotherms of the CNT layers was studied. The optimal value of the volume of the working solution $V_{\text{CNT}} = 200$ μL was experimentally determined for obtaining the most uniform layers on the surface of water and films on a solid substrate, which at the same time have the highest conductivity. The study also revealed an increase in the number of nanotube aggregates with an increase in the amount of the working solution. When forming layers from mixtures of CNTs and AA, various ratios of volumes $V_{\text{CNT}} : V_{\text{AA}}$ were tested – 100 : 0, 95 : 5, 90 : 10, 80 : 20, 70 : 30, 50 : 50, 30 : 70, 10 : 90, 0 : 100, of which the variant with the optimal ratio (80 : 20) was selected, at which the AA amount was minimal and sufficient for assessing the degree of compression of the formed layer. It was found that adding arachidic acid to the CNT solution in an amount of 20 % of the total volume leads to an increase in the conductivity of the film obtained on the basis of this mixture by more than 2 orders of magnitude. The most probable reason for such an increase in conductivity may be an increase in the degree of ordering and packing density of CNTs upon adding a small amount of surfactant – arachidic acid.

Thus, in the course of the research, elements of the Langmuir-Blodgett technology were developed, allowing for the production of thin conducting CNT films with the average values of sheet conductance and sheet resistance were $G_{sh} = 1.18 \cdot 10^{-3}$ S·sq^{-1} and $R_{sh} = 847$ Ohm·sq^{-1}, respectively. The results obtained are interesting not only from a purely scientific point of view, but also from the point of view of the practical application of such films in devices for various purposes, in particular, in flexible and wearable electronics.

5. Funding

The study was supported by the Russian Science Foundation (project No. 21-73-20057) and Saratov State University, Russia.

6. Conflict of interest

The authors declare no conflicts of interest.

References

1. Bauhofer W, Kovacs JZ. A review and analysis of electrical percolation in carbon nanotube polymer composites. *Composites Science and Technology*. 2009;69(10):1486-1498. DOI:10.1016/j.compscitech.2008.06.018

2. Jia L, Zhang Y, Li J, You C, et al. Aligned single-walled carbon nanotubes by Langmuir–Blodgett technique. *Journal of Applied Physics*. 2008;104(7):074318. DOI:10.1063/1.2996033

3. Saito R, Dresselhaus G, Dresselhaus MS. *Physical properties of carbon nanotubes*. Tokyo:Imperial College Press; 1998. 272 p. DOI:10.1142/p080

4. Sun X, Li R, Stansfield B, Dodelet JP, et al. 3D carbon nanotube network based on a hierarchical structure grown on carbon paper backing. *Chemical Physics Letters*. 2004;394(4-6):266-270. DOI:10.1016/j.cplett.2004.07.014

5. Lu R, Christianson C, Weintrub B, Wu JZ. High photoresponse in hybrid graphene–carbon nanotube infrared detectors. *ACS Applied Materials & Interfaces*. 2013;5(22):11703-11707. DOI:10.1021/am4033313

6. Lu R, Christianson C, Kirkeminde A, Ren S, et al. Extraordinary photocurrent harvesting at type-II heterojunction interfaces: toward high detectivity carbon nanotube infrared detectors. *Nano Letters*. 2012;12(12): 6244-6249. DOI:10.1021/nl303302p

7. Itkis ME, Borondics F, Yu A, Haddon RC. Bolometric infrared photoresponse of suspended single-walled carbon nanotube films. *Science*. 2006;312(5772): 413-416. DOI:10.1126/science.1125695

8. Ali A, Rahimian Koloor SS, Alshehri AH, Arockiarajan A. Carbon nanotube characteristics and enhancement effects on the mechanical features of polymer-based materials and structures – a review. *Journal of Materials Research and Technology*. 2023;24:6495-6521. DOI:10.1016/j.jmrt.2023.04.072

9. Wu J, Lan Z, Lin J, Huang M, et al. Counter electrodes in dye-sensitized solar cells. *Chemical Society Reviews*. 2017;46(19):5975-6023. DOI:10.1039/C6CS00752J

10. *IEEE International roadmap for devices and systems: 2017 edition*. Available from: https://irds.ieee.org/editions/2017 [Accessed: 3 December 2024].

11. Venkataraman A, Amadi EV, Chen Y, Papadopoulos C. Carbon nanotube assembly and integration for applications. *Nanoscale Research Letters*. 2019;14(1):220. DOI:10.1186/s11671-019-3046-3

12. Moriarty P. Nanostructured materials. *Reports on Progress in Physics*. 2001;64(3):297-381. DOI:10.1088/0034-4885/64/3/201

13. Huang KC, Wang YC, Dong RX, Tsai WC, et al. A high performance dye-sensitized solar cell with a novel nanocomposite film of PTNP/MWCNT on the counter electrode. *Journal of Materials Chemistry*. 2010;20(20): 4067. DOI:10.1039/b925245b

14. Oliveira ON, Caseli L, Ariga K. The past and the future of Langmuir and Langmuir–Blodgett films. *Chemical Reviews*. 2022;122(6):6459-6513. DOI:10.1021/acs.chemrev.1c00754

15. Adamson AW, Gast AP. *Physical chemistry of surfaces*. New York: Wiley; 1997. 784 p.

16. Petty MC. *Langmuir-Blodgett films: An introduction*. New York: Cambridge University Press; 1996. 234 p.

17. Gorbachev IA, Gluhovskoy EG. The studying of components ratio influence in mixed monolayers of quantum dots and arachidic acid on the films morphology based on them. *Izvestiya Saratovskogo universiteta. Novaya seriya. Seriya: khimiya. biologiya. ekologiya*. 2018;18(3):299-305. DOI:10.18500/1816-9775-2018-18-3-299-305 (In Russ.)

18. Gorbachev I, Smirnov A, Ivanov G, Avramov I, et al. Langmuir-Blodgett films of arachidic and stearic acids as sensitive coatings for chloroform hf saw sensors. *Sensors*. 2022;23(1):100. DOI:10.3390/s23010100

19. Hadjichristov GB, Marinov YG, Vlakhov TE, Scaramuzza N. Phospholipid Langmuir-Blodgett nano-thin monolayers: electrical response to cadmium ions and harmful volatile organic compounds. In: *Advances in Biomembranes and Lipid Self-Assembly*. Elsevier; 2021. p. 129-172. DOI:10.1016/bs.abl.2021.11.005

20. Zubova KV, Kuznetsova VA, Al-Alwani AJK, Glinskaya EV, et al. Characteristics of Langmuir monolayers of phospholipids isolated from the cell membranes of the E. coli K-12 test culture. *Aktual'nyye voprosy biologicheskoy fiziki i khimii*. 2021;6(2):285-288. (In Russ.)

21. Klimov BN, Glukhovskoy EG. Visualization of the structure of Langmuir-Blodgett films in liquid crystal cells. *Zhurnal tekhnicheskoy fiziki = Technical Physics*. 2002;72(12):94-97. (In Russ.)

22. Al-Alwani AJK, Chumakov AS, Kolesnikova AS, Pozharov MV, et al. Investigation of the properties of semiconductor quantum dots on dielectric Langmuir monolayers. *Izvestiya Yugo-Zapadnogo gosudarstvennogo universiteta. Seriya: Tekhnika i tekhnologii.* 2019;9(1)(30):56-67. (In Russ.)

23. Mironyuk VN, Al-Alwani AJK, Karatyshova TYa, Smirnova AI, et al. Influence of subphase temperature on Langmuir layers and thin films of A3B-type porphyrine derivative. *Surfaces and Interfaces*. 2024;52:104880. DOI:10.1016/j.surfin.2024.104880

24. Al-Hassani AJR, Al-Alwani AJ, Mironyuk VN, Pozharov MV. Miscibility of porphyrin/liquid crystal floating monolayers at the air–water interface. *Phase Transitions*. 2024;97(3):192-200. DOI:10.1080/01411594.2023.2301465

25. Wu Y, Liu Z, Zhou S, Wang F, et al. Langmuir-Blodgett assembly of carboxylic multiwalled carbon nanotubes-nafion for amperometric sensing of codeine. *Journal of The Electrochemical Society*. 2019;166(13): H592-H597. DOI:10.1149/2.0371913jes

26. Matsui J, Iko M, Inokuma N, Orikasa H, et al. Fabrication of carbon nanotube Langmuir-Blodgett film by polyion complex method. In: *Materials Research Society Symposium Proceedings*. 2006;963:208-211. DOI:10.1557/PROC-0963-Q05-35

27. Hrushevsky VV, Krylova HV, Lipnevich IV, Shulitsky BG, et al. Clusterization and spontaneous polarization in thin Langmuir – Blodgett films with modified multi-walled carbon nanotubes. *Proceedings of the "Foundations & Advances in Nonlinear Science" Conference-School*. Minsk: Belarusian State University; 2009. p. 50-60.

28. Lo CL, Lee YL, Hsu WP. Behavior of mixed multi-walled carbon nanotube/p3ht monolayer at the air/water interface. *Synthetic Metals*. 2010;160(19-20): 2219-2223. DOI:10.1016/j.synthmet.2010.08.014

29. *Multi walled carbon nanotubes for research and commercial applications.* Available from: https://www.ctimaterials.com/product-category/multi-walled-carbon-nanotubes/ [Accessed: 3 December 2024].

30. Tajuelo J, Guzmán E, Ortega F, Rubio RG, et al. Phase diagram of fatty acid Langmuir monolayers from rheological measurements. *Langmuir*. 2017;33(17):4280-4290. DOI:10.1021/acs.Langmuir.7b00613

31. Lvov YuM, Feigin LA. Langmuir films production, structure, some applications. *Kristallografiya = Soviet Physics. Crystallography*. 1987;32(3):800-815. (In Russ.)

32. Moehwald H, Brezesinski G. From Langmuir monolayers to multilayer films. *Langmuir*. 2016;32(41):10445-10458. DOI:10.1021/acs.Langmuir.6b02518

33. Ngoma MM, Mathaba M, Moothi K. Effect of carbon nanotubes loading and pressure on the performance of a polyethersulfone (PES)/carbon nanotubes (CNT) membrane. *Scientific Reports*. 2021;11(1):23805. DOI:10.1038/s41598-021-03042-z

Information about the authors / Информация об авторах

Oday A. H. Hassoon, Engineer, Saratov State University (SSU), Saratov, Russian Federation; Engineer, Ministry of Electricity, Baghdad, Iraq; ORCID 0009-0009-5404-6622; e-mail: uday_m82@yahoo.com

Odai N. Salman, Cand. Sc. (Eng.), Associate Professor, University of Technology, Baghdad, Iraq; ORCID 0000-0002-0485-667X; e-mail: Odai.N.Salman@uotechnology.edu.iq

Tatiana Ya. Karatyshova, Engineer, SSU, Saratov, Russian Federation; ORCID 0000-0001-9546-3646; e-mail: tatochka338@gmail.com

Ammar J. K. Al-Alwani, Cand. Sc. (Phys. and Math.), Engineer, SSU, Saratov, Russian Federation; Lecturer, Al-Furat Al-Awsat Technical University, Technical Institute Kufa, Kufa, Iraq; ORCID 0000-0002-5665-464X; e-mail: ammarhamlet2013@yahoo.com

Maxim V. Gavrikov, Engineer, SSU, Saratov, Russian Federation; ORCID 0000-0002-1438-3060; e-mail: maks.gavrikov.96@gmail.com

Vladislav N. Mironyuk, Engineer, SSU, Saratov, Russian Federation; ORCID 0000-0001-5078-5422; e-mail: bestblogger@yandex.ru

Andrey M. Zakharevich, Cand. Sc. (Phys. ans Math.), Head of Laboratory, SSU, Saratov, Russian Federation; ORCID 0000-0002-3813-5870; e-mail: lab-15@mail.ru

Mikhail V. Pozharov, Cand. Sc. (Chem.), Associate Professor, SSU, Saratov, Russian Federation; ORCID 0000-0003-2914-7260; e-mail: pozharovmv@gmail.com

Evgeny G. Glukhovskoy, Cand. Sc. (Phys. ans Math.), Head of Laboratory, SSU, Saratov, Russian Federation; ORCID 0000-0002-8282-3638; e-mail: glukhovskoy@gmail.com

Хассун Одай Али Хассун, инженер, Саратовский национальный исследовательский государственный университет имени Н. Г. Чернышевского (СГУ), Саратов, Российская Федерация; инженер, Министерство электроэнергетики, Багдад, Ирак; ORCID 0009-0009-5404-6622; e-mail: uday_m82@yahoo.com

Салман Одай Наеем, кандидат технических наук, доцент, Технологический университет, Багдад, Ирак; 0000-0002-0485-667X; e-mail: Odai.N.Salman@uotechnology.edu.iq

Каратышова Татьяна Яковлевна, инженер, СГУ, Саратов, Российская Федерация; ORCID 0000-0001-9546-3646; e-mail: tatochka338@gmail.com

Аль-Алвани Аммар Жабер Кадим, кандидат физико-математических наук, инженер, СГУ, Саратов, Российская Федерация; преподаватель, Аль-Фурат Аль-Авсат Технический университет, Технический институт Куфа, Куфа, Ирак; ORCID 0000-0002-5665-464X; e-mail: ammarhamlet2013@yahoo.com

Гавриков Максим Владимирович, инженер, СГУ, Саратов, Российская Федерация; ORCID 0000-0002-1438-3060; e-mail: maks.gavrikov.96@gmail.com

Миронюк Владислав Николаевич, инженер, СГУ, Саратов, Российская Федерация; ORCID 0000-0001-5078-5422; e-mail: bestblogger@yandex.ru

Захаревич Андрей Михайлович, кандидат физико-математических наук, заведующий лабораторией, СГУ, Саратов, Российская Федерация; ORCID 0000-0002-3813-5870; e-mail: lab-15@mail.ru

Пожаров Михаил Владимирович, кандидат химических наук, доцент, СГУ, Саратов, Российская Федерация; ORCID 0000-0003-2914-7260; e-mail: pozharovmv@gmail.com

Глуховской Евгений Геннадьевич, кандидат физико-математических наук, заведующий лабораторией, СГУ, Саратов, Российская Федерация; ORCID 0000-0002-8282-3638; e-mail: glukhovskoy@gmail.com

Received 16 January 2025; Revised 06 February 2025; Accepted 12 February 2025