

CHEMISTRY. CHEMICAL ENGINEERING**ХІМІЯ. ХІМТЕХНОЛОГІЯ**

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THE ACTION OF A PLASMA DISCHARGE AND THEIR
ANTIMICROBIAL PROPERTIES: FORMATION
OF CLUSTERS AND SILVER PARTICLES**

M.I. Skiba, O.A. Pivovarov, V.I. Vorobyova. **Одержання наночастинок срібла під дією плазмового розряду та їх антимікробні властивості: формування кластерів та часток срібла.** Розглянуто одержання водних розчинів наночастинок срібла із застосуванням розряду контактної нерівноважної низькотемпературної плазми. Метою роботи є дослідження формування кластерів та часток срібла в водних розчинах під дією розряду плазми. Для визначення термодинамічних величин утворення кластерів срібла використовували метод квантової механіки, зокрема теорію функціоналу густини. Термодинамічний потенціал формування наночастинок срібла у водному середовищі визначали за рівнянням Нернста. Дослідження проводили в газорідному реакторі періодичної дії об'ємом 100 мл. Тиск в реакторі становив 80 ± 4 кПа. Силу струму підтримували на рівні 120 ± 6 мА. Час плазмової обробки розчинів варіювали в діапазоні від 10 с до 7 хв. Розчини готували шляхом розчинення нітрату аргентуму у дистильованій воді в заданому співвідношенні. Спектри колоїдних розчинів отримували на спектрофотометрі UV-5800PC з використанням кварцових кювет в діапазоні довжин хвиль 190...700 нм. Розподіл розмірів частинок визначали за допомогою аналізатора розмірів частинок Zetasizer Nano ZS. Експериментально і теоретично встановлено, що позитивно заряджені кластери структури Ag_4^{+2} та Ag_8^{+2} термодинамічно найбільш вірогідніші та передують утворенню наночастинок срібла в результаті дії розряду плазми на водний розчин нітрату аргентуму. Встановлено, що на початкових етапах (до 10 сек.) плазмової обробки водного розчину нітрату срібла формуються кластери структури Ag_4^{+2} та Ag_8^{+2} з характерними піками $\lambda_{max}=265...325$ нм; від 10 сек до 7 хв відбувається формування НЧ срібла з піками $\lambda_{max}=430...440$ нм. Досліджено кінетику хімічних перетворень у водних розчинах при плазмохімічній обробці водних розчинів нітрату срібла. Встановлено, що процес плазмохімічного формування наночастинок срібла є реакцією першого порядку. Визначено антимікробну активність розчину НЧ по відношенню до грам негативного тест-мікроорганізму *E. coli*.

Ключові слова: наночастки, срібло, плазма, квантово-хімічний розрахунок, кластери, термодинамічний потенціал, антимікробна активність

M. Skiba, A. Pivovarov, V. Vorobyova. **Preparation of silver nanoparticles under the action of a plasma discharge and their antimicrobial properties: formation of clusters and silver particles.** The obtaining of aqueous solutions of silver nanoparticles using a discharge of contact nonequilibrium low-temperature plasma is considered. The aim is to study the formation of clusters and silver particles in aqueous solutions under plasma discharge. The method of quantum mechanics, namely the theory of density functional, was used to determine the thermodynamic values of the formation of clusters of silver. The standard Gibbs free energy of formation of silver nanoparticles was calculated according to the Nernst equation. The investigations were carried out in a gas-liquid batch reactor with volume of 100 ml. The reactor pressure was 80 ± 4 kPa. The current was maintained at 120 ± 6 mA. The time of treatment was from 10 seconds till 14 minutes. The solutions were prepared by dissolving the argentums nitrate in distilled water with a predetermined ratio. Optical spectra of sols were recorded on the spectrophotometer UV-5800PC in the wavelength range 190...700 nm. Particle size of colloidal solutions was measured by means of the analyzer of particle size Zetasizer Nano-25 (Malvern Instruments Ltd., Malvern, England). Applying experimental and theoretical methods it was established that positively charged clusters of Ag_4^{+2} and Ag_8^{+2} structures are thermodynamically most probable and precede the formation of silver nanoparticles under the action of plasma discharge on an aqueous solution of silver nitrate. It was established that in the initial stages (up to 10 sec) the silver clusters of Ag_4^{+2} and Ag_8^{+2} structures with characteristic peaks $\lambda_{max}=265...325$ nm are formed in silver nitrate aqueous solution under plasma discharge treated; silver nanoparticles with peaks λ_{max} at 430...440 nm are formed after 10 sec – 7 minutes of processing. The kinetics of chemical transformations in aqueous solutions during plasma-chemical treatment of aqueous solutions of silver nitrate was studied. It was established that the process of plasma-chemical formation of silver nanoparticles is a first-order reaction. The antimicrobial activity of nanoparticles solution in relation to Gram-negative bacteria *E. coli* test microorganism was determined.

Keywords: nanoparticles, silver, plasma, quantum-chemical calculation, clusters, thermodynamic potential, antimicrobial activity

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Introduction. Today one of the widely studied types of nanomaterials is silver nanoparticles (Ag NP) [1]. This is due to their polyfunctional properties [2]. It has now been reliably established that Ag NP exhibits antimicrobial, antifungal, antiviral, catalytic and other properties. This determines the possibility of their practical application in various fields: water purification and water treatment, textile, food, chemical, medicine, etc.

Analysis of recent research and publications. Currently, there is a wide range of methods for synthesizing of silver nanoparticles that allow the formation of stable dispersions of Ag NP [3]. With all their advantages, most of the existing methods require the use of toxic reagents-reducing agents / stabilizers, maintaining the temperature regime, implementing several technological steps, etc. [1 – 4]. In view of this, the development of productive, environmentally safe and economically feasible methods of nanoparticle synthesis, which reduces the amount of reagent components and replaces toxic components, is extremely important now. Promising and competitive processes are the processes based on plasma technologies using different plasma formation units. In a number of papers reported the possibility of obtaining nanoparticles of metals and oxides directly by means of a plasma discharge, which is generated between electrodes immersed in a liquid [5, 6, 7], at the boundary between the phases of the gas-liquid at reduced pressure [8], the atmospheric pressure plasma in interaction with liquid [9] and others. Among plasmochemical discharges, the contact nonequilibrium low-temperature plasma (CNP) is perspective in terms of practical application. The plasma discharge is generated between the electrode located in the gas phase and the liquid surface in the volume of which is the second electrode. Variation of the composition of liquid phases may control the routes of chemical transformation and the composition of the resulting products [10]. In previous papers, the authors have shown the effectiveness of using low-temperature contact nonequilibrium plasma (CNP) to obtain nanoparticles of silver from aqueous solutions of metal salt in one technological step without the use of additional reagents-reducing agents [11, 12, 13].

Problem statement. It is now known that the formation of nanosheets of silver occurs through the formation of silver clusters of different structures [14, 15]. Their structure, organization and duration of existence are conditioned by the conditions of receipt (precursor / reducing agent / stabilizer). A series of theoretical and practical works are devoted to the construction of silver clusters and their properties [16, 17, 18]. Therefore, it is of scientific and practical interest to investigate the early stages of plasma-chemical formation of nanosheets of silver and the further formation of nanosheets of silver.

The purpose of this work is to study the formation of clusters and silver particles in aqueous solutions of silver nitrate under the action of a discharge of contact nonequilibrium low-temperature plasma.

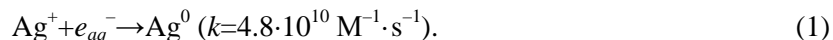
Experiment Methodology. To determine the thermodynamic values of the formation of silver clusters of, we used the method of quantum mechanics, in particular the theory of functional density. The calculations were carried out using a non-empirical method using quantum-chemical calculations in the GAUSSIAN program. The visualization of the results was carried out in the GaussView program. The calculations were carried out in the basis of LANL2DZ. All calculations were carried out in a mode of full optimization of the geometric position of each atom of the investigated system. For theoretical calculation of the formation of clusters of different structures, Gibbs energy was calculated (kcal/mole (kJ/mol) $\Delta G = G_{\text{products}} - G_{\text{reagents}}$.

Silver solutions were prepared by dissolution of nitrogen argentum (AgNO₃) P.A. in distilled water. The obtained solutions of a certain concentration were treated in a reactor with a discharge of contact nonequilibrium low-temperature plasma. The research was carried out in a gas-liquid reactor of 100 milliliters periodic action. Used electrodes made of stainless steel X18H10T. The cathode ($d=4$ mm) is located in the liquid part, and the anode ($d=2.4$ mm) at a distance of 10 mm from the surface of the solution. The volume of the solution in the reactor was 70 ml. Cooling of the reaction mixture provided a continuous circulation of cold water. Pressure in the reactor is 80 ± 4 kPa. For obtaining a plasma discharge on the electrodes, a voltage of 500...1000 V. voltage was maintained at a level of 120 ± 6 mA. Plasma processing time of solutions was up to 1 min. After plasma treatment, the resulting solutions were cooled to room temperature.

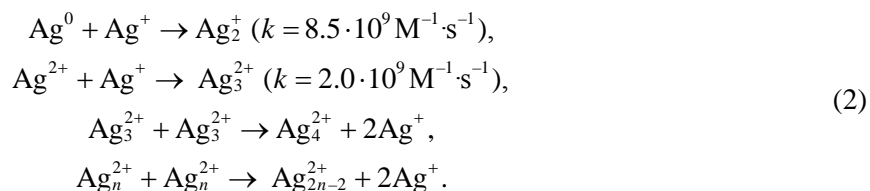
To characterize the formed silver clusters/nanosheets of silver, after analysis the reaction mixture was analyzed using spectrophotometry. The spectra of colloidal solutions were obtained on a spectrophotometer UV-5800PC using a quartz cell in the wavelength range of $\lambda=300\text{...}700$ nm. Peaks at $\lambda=260\text{...}335$ nm testify to the formation of clusters of silver of different structures, and the peak at $\lambda=400\text{...}440$ nm on the formation of Ag NP. The particle size distribution was determined using Zetasizer Nano ZS (Malvern Instruments Ltd, United Kingdom) particle size analyzer. Electron microscopic studies of colloidal silver dispersion samples were carried out using the TEM JEOL JEM 200 CX transmissive electron microscope. The yield of nanosheets of silver was estimated by the difference of the argon ions in the initial solution and after processing with plasma discharge. To measure the application of ion-selective electrode of ions of the "ELIS-131Ag".

Tests for the determination of the antimicrobial activity of solutions of silver NP by the suspension method were performed under the following conditions. As a test microorganism, *E. coli* at a concentration of 10^4 CFU/cm³ was used to determine the antimicrobial action of the colloidal solution of nanosilver. The duration of the exposure of the experiment was 5 minutes, 1, 2, 3 hours. During the test, 0.1 cm³ suspensions of the test microorganism were introduced in 5 cm³ of each test specimen. Solution samples were incubated at (20 ± 1) °C. At the end of the exposure time, 0.5 cm³ specimens were hanging on two Petri dishes with a dense nutrient medium incubated at 36 °C for 24 hours. For each breeding, the amount of CFU/cm³ was calculated. The results of tests of colloidal solution of nanosilver were compared with the results of culture control *E. coli*, conducted in a similar way to the experiment.

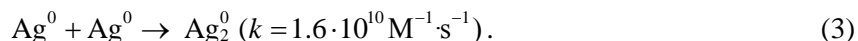
Results and discussion. At present, it is reliably found that, under certain experimental conditions [14 – 18], the atoms and metal ions are chemically active particles and when interacting with each other and the ions present form short-lived, small positively charged or neutral clusters. If the solution contains ions of the same metal, then there are homoelectric clusters. Positively charged clusters are formed in solutions containing an excess of metal ions compared with the concentration of radicals–reducing agents. The conditions for the formation of silver clusters are discussed in detail in [14 – 18]. It is reported that in the reaction of silver ions with hydrated electrons Ag^0 :



The formation of the NP is possible as a result of the interaction of Ag^0 atoms with Ag^+ through positively charged clusters:



Also, the formation of clusters is possible as a result of the interaction of atoms Ag^0 :



In both cases, besides positively charged clusters, it is possible to form and neutral silver clusters (Ag_3 , Ag_6 and Ag_{13}) when the concentration of reducing radicals exceeds the concentration of Ag^+ ions. As a result of "clumping" of clusters quasimetal and nanosized silver particles are formed.

To date, a computational experiment aimed at the study of silver clusters relies on several groups of computational methods: molecular mechanics, molecular dynamics methods (MD), and empirical and semiempirical quantum–mechanical methods (QMM). In a number of papers [14 – 18], by means of quantum–chemical calculations, thermodynamic properties, correlation of optical and electronic properties of positively charged clusters of silver are established. It is worth noting that in the QMM for calculating the energies of the main and excited states it is expedient to apply DFT–methods in which, instead of wave functions, calculations use electronic densities. The widespread use of this

method is due to the possibility of obtaining theoretically calculated parameters (thermodynamic and energy) for the formation of clusters and nanoscale silver.

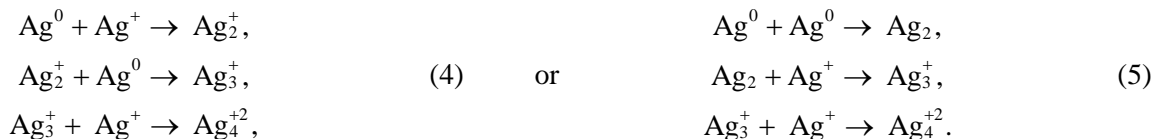
The method of quantum-chemical calculations has established the possibility of forming clusters of silver of different composition. Calculations were made on the assumption of the formation of silver clusters as a result of the interaction of Ag^0 atoms with Ag^+ ions and Ag^0 atoms. The Gibbs free energy value is calculated for the most probable clusters. The results of calculations are shown in the Table 1.

Table 1

The value of the Gibbs free energy of Ag_n clusters ((n) 2–4)) for Ag^0 and Ag^+ and two Ag^0 atoms

No	The type of reaction	Free Gibbs energy kcal/mole	The type of reaction	Free Gibbs energy kcal/mole
$Ag^0 + Ag^+$			$Ag^0 + Ag^0$	
1	$Ag^0 + Ag^+ \rightarrow Ag_2^+$	-31.6	$Ag^0 + Ag^0 \rightarrow Ag_2$	-30.1
2	$Ag_2^+ + Ag^+ \rightarrow Ag_3^{2+}$	+141.2	$Ag_2 + Ag^+ \rightarrow Ag_3^+$	-55.6
	$Ag_2^+ + Ag^0 \rightarrow Ag_3^+$	-52.9	$Ag_2 + Ag^0 \rightarrow Ag_3$	-12.1
3	$Ag_3^{2+} + Ag^+ \rightarrow Ag_4^{3+}$	Not stable	$Ag_3^+ + Ag^+ \rightarrow Ag_4^{2+}$	-55.1
	$Ag_3^{2+} + Ag^0 \rightarrow Ag_4^{2+}$	-139.4	$Ag_3^+ + Ag^0 \rightarrow Ag_4^{2+}$	-16.0
4	$Ag_3^+ + Ag^+ \rightarrow Ag_4^{2+}$	-16.7	$Ag_3 + Ag^0 \rightarrow Ag_4$	-27.0
	$Ag_3^+ + Ag^0 \rightarrow Ag_4^+$	+55.5	$Ag_3 + Ag^+ \rightarrow Ag_4^+$	-60.1

Estimated data indicate the possibility of forming stable dimers (Ag_2^+), trimers (Ag_3^+) and tetramers (Ag_4^+). It is established that the charge placed in nanoparticles is a key factor determining the selectivity of different paths for the formation of clusters. According to the calculated data obtained, as in the case of the interaction of Ag^0 and Ag^+ , and with two Ag^0 atoms, the most probable is the formation of Ag_4^{+2} and Ag_8^{+2} clusters:



It is now firmly established that the action of a plasma discharge on an aqueous electrolyte solution causes the dissociation and ionization of water molecules and initiates the appearance in the region of the interface between the plasma-liquid phases of primary active particles such as atomic hydrogen, hydroxyl radicals, and solvated electrons. The potential E_0 of the Ag^+/Ag^0 pair is -1.8 V. Therefore reactive compounds can carry out a single electron recovery of Ag^+ ions.

Theoretically calculated data on the formation of silver clusters is confirmed by the results of experimental studies. The results are shown in Fig. 1.

The formation of silver clusters under conditions of plasma discharge on aqueous solutions of silver nitrate was carried out at a different initial concentration of silver nitrate and the duration of processing by discharging. It is known that clusters of silver, as well as NP silver, are characterized by the formation of a peak of plasmon resonance at a length $\lambda=260...330$ nm. For all investigated initial concentrations of silver in the treated

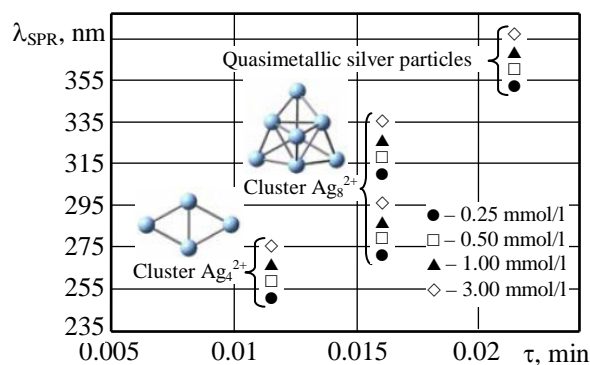


Fig. 1. The dependence of the surface plasmon resonance peak (SPR) on the duration of the plasma discharge and the concentration of nitrate of the argentum in the treated solution

solution with a duration of discharge of 4 sec on the spectra, a peak of the surface plasmon resonance SPR is formed at $\lambda=265\dots280$ nm, which is known [14 – 18], characteristic cluster of Ag_4^{2+} composition. An increase in the duration of plasma processing up to 6 sec causes the formation of a pair of peaks of SPR at $\lambda=282\dots320$ nm, which belongs to clusters of Ag_8^{2+} structure. It should be noted that the formation of Ag_8^{2+} clusters is accompanied by the disappearance of Ag_4^{2+} clusters. The obtained data are consistent with the results of other researchers [19], which indicate that the duration of its existence is 1 sec. Subsequent irradiation is accompanied by the disappearance of the Ag_8^{2+} cluster and the formation of a peak of SPR of quasimetallic particles (360...380 nm).

Thus, the set of experimental and estimated data shows that in the conditions of plasmachemical processing of aqueous solution of silver nitrate by plasma dissociation, the formation of two types of Ag_4^{2+} and Ag_8^{2+} clusters with the subsequent formation of quasimetallic nanoparticles of silver is observed. The thermodynamic stability of these types of clusters is currently investigated in works [14 – 17] and is explained by the geometric and energy parameters of these clusters (high symmetry, high values of ionization energy, lower values of the energy of electron affinity, etc.).

As noted above, the final result of the formation and interaction of clusters and/or ions is the formation of metallic nanoparticles of silver. The thermodynamic potential of formation of nanosheets of silver in an aqueous medium is one of the main parameters for assessing the physical and chemical behavior of silver nanoparticles. The analysis of literature points to differences in approach to the calculation of ΔG^0 AgNP in the aquatic environment. For nanoparticles of size (5...25 nm), the thermodynamic potential in an aqueous medium can be calculated according to the Nernst equation [20].

$$\Delta G_{f(\text{AgNP}_s)}^0 = -Z \cdot F \cdot E + 77.120, \quad (6)$$

where Z – number of electrons;

F – constant Faraday, 96485.55 C/mol;

E – electrode potential, V [21];

77.120 – standard Gibbs formation energy Ag_{aq}^+ , kJ/mole.

The calculation results are presented in Table 2.

Table 2

Calculated Gibbs energy for obtaining nanosheets
of silver in an aqueous medium with a different particle radius

$r_{\text{AgNP}}, \text{ nm}$	$\Delta E, \text{ V}$	$E, \text{ V}$	$\Delta G_{f(\text{AgNP}_s)}^0, \text{ J/mol}$
5	-0.12	0.262	51.84
10	-0.07	0.312	47.016
15	-0.038	0.344	43.92
20	-0.011	0.371	41.32
22	-0.0003	0.381	40.29

The obtained data show the pattern: the free energy of Gibbs, the formation of nanoparticles in aqueous solutions increases with decreasing the size of silver particles. The obtained data are theoretically calculated and therefore only the thermodynamic probability of forming different nanoscale sizes according to the accepted conditions (temperature, shape of particles, etc.) is determined.

Since the properties of nanosystems depend on the dimensional characteristics of nanoparticles, the control of their morphology and size is an important task. Experimental data (Table 3) show that the average diameter of nanosheets formed under the action of a plasma discharge is 36.5...60.1 nm and increases with an increase in the initial concentration of Ag^+ in the treated solution (The samples were subjected to the following conditions: the duration of synthesis 5 min, $I=120$ mA). The results of electron microscopy studies (Fig. 2) show that the nanoparticles formed are mainly spherical.

Table 3

The size of silver nanoparticles obtained in plasma processing (experimental data)

C AgNO ₃ , mmol/l	d _{AgNP} , nm
0.25	36.5±1.2
0.5	38.0±2.3
1.0	50.1±2.7
3.0	60.1±2.0

The formation of silver nanoparticles by restoring Ag⁺ ions by reducing agents is described by the law of velocity:

$$v = \frac{dC(\text{Ag}^0)}{dt}, \quad (7)$$

where c(Ag⁰) – concentration of silver nanoparticles over time t.

Assuming that C (oxidant) >> C(Ag⁺), equation (7) can be written as follows:

$$v = \frac{dC(\text{Ag}^0)}{dt} = kc(\text{Ag}^+), \quad (8)$$

where k – imaginary constant of the reaction rate; c(Ag⁺) t is the concentration of silver ions at time t.

Thus, to determine the order of the recovery reaction, the dependence of the concentration on the velocity (C(Ag⁺)-v) or concentration on time (C(Ag⁺)-τ) should be investigated. The formation of NP in an aqueous solution under conditions of plasma discharge is investigated. The change in the equilibrium concentration of argon ions depending on the duration of the plasma discharge is studied at different initial concentrations of the argon ions in the solution. The obtained data is shown in Fig. 3.

According to the experimental data, the rate constant of the plasma-chemical formation of nanosheets of silver is a reaction of the first order (Fig. 4) and is 0.4...0.41 min⁻¹.

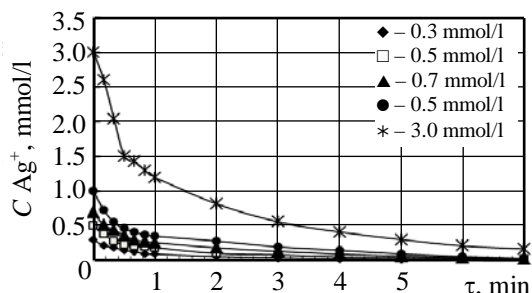


Fig. 3. Change in the concentration of Ag⁺ depending on the duration of the plasma discharge at different initial concentrations of silver ions in the treated solution

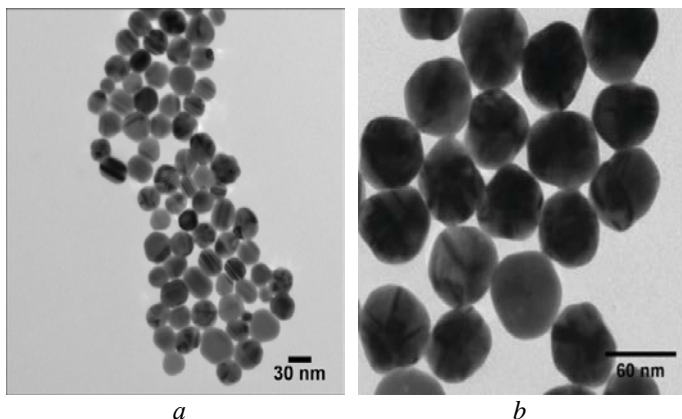


Fig. 2. TEM photographs of silver nanoparticles obtained by plasmochimic method at concentration of AgNO₃, mmol/l: 0.25 (a), 3.0 (b)

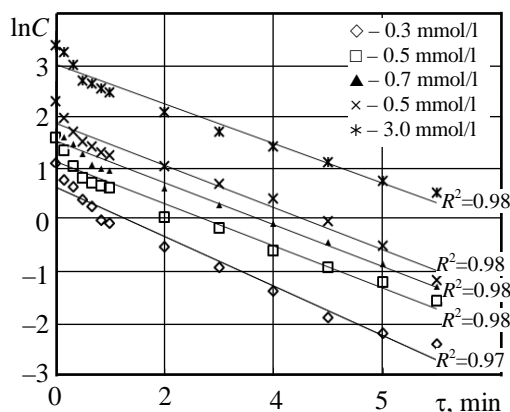


Fig. 4. Dependence of the logarithm of the equilibrium concentration of Ag⁺ depending on the duration of the plasma discharge at different initial concentrations of silver ions in the solution

Table 4

Determination of the antimicrobial activity of the NP solution in relation to the test-microorganism *E. coli* by the suspension method

Time of exposition	Concentration of nanosilver ($\mu\text{g}/\text{sm}^3$), CFU/cm ³			Control of <i>E. coli</i> culture
	35.0	20.0	10.0	
5 min	0	50	55	65
1 h	0	10	17	61
2 h	0	9	14	62
3 h	0	0	5	63
12 h	0	0	0	64

Silver nanoparticles have a number of different pharmacological effects. The main among them is antimicrobial. The antimicrobial activity of a plasmochemically obtained colloidal solution of nanosilver was studied. For the study, samples of NP Ag 1.0 mol/l were used for plasma 1 min. The results are presented in Table 4.

The experimental studies on the determination of the antimicrobial activity of the colloidal NP solution indicate that the *E. coli* test microorganism is sensitive to the action of obtained plasma-chemically obtained silver nano dispersions at concentrations of 10 to 35 $\mu\text{g}/\text{sm}^3$. Exposure for 12 hours caused a bactericidal effect on the test microorganism. During this time there

was a steady 100 % reduction of microbial load compared with control samples. At the same time it can be seen that in order to achieve a decrease in microbial load in a short-term exposure period (5 min), it is necessary to use nanosheets of silver at a concentration of not less than 35.0 $\mu\text{g}/\text{cm}^3$. For a concentration of 20 $\mu\text{g}/\text{sm}^3$, the minimum exposure time is 2...3 h.

To date, researchers note the following mechanism of antimicrobial action of nanosilver [22]:

1. Silver nanoparticles are adsorbed on the surface of the membrane of microorganisms;
2. Nanoparticles destroy the molecules of the lipopolysaccharide, accumulate inside the membrane, form "cells" and increase the permeability of the membrane.

Silver nanoparticles penetrate inside the cell of the microorganism with the release of silver ions Ag^+ , causing the following effects:

- silver ions bind to cytochromes and block the respiratory chain;
- silver ions bind to the components of the electron transport chain, as well as DNA, suppressing its replication.

Conclusions

The obtaining of aqueous solutions of nanosheets of silver with the use of the discharge of contact nonequilibrium low-temperature plasma is considered. The thermodynamic calculation of Gibbs free energy of the formation of silver clusters and silver nanoparticles has made. Theoretical calculations show that positively charged Ag_4^{+2} and Ag_8^{+2} clusters are thermodynamically most probable and precede the formation of nanoparticles of silver as a result of the plasma discharge on an aqueous solution of nitrate argentum. It has been experimentally established that clusters of silver of Ag_4^{+2} and Ag_8^{+2} structures with characteristic peaks $\lambda_{\text{mak}}=265...325$ nm are formed at the initial stages (up to 10 seconds) of plasma processing of the aqueous solution of nitrate of the argentum. The following regularity is established: the free energy of Gibbs for the formation of nanosheets of silver in aqueous solutions increases with decreasing the size of silver particles. It is established that for 10 sec – 7 minutes of plasma processing of nitrate Ag solution the low-frequency silver with peaks $\lambda_{\text{mak}}=430...440$ nm is forming. The kinetics of chemical transformations in aqueous solutions during plasmochemical treatment of aqueous solutions of silver nitrate was studied. It was established that the process of plasmochemical formation of nanosheets of silver is a first-order reaction. The antimicrobial activity of the NP solution in relation to the gram of the negative test-microorganism *E. coli* is determined.

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