PLASMOCHEMICAL PREPARATION OF SILVER NANOPARTICLES: THERMODYNAMICS AND KINETICS ANALYSIS OF THE PROCESS

Здійснено термодинамічний розрахунок вільної енергії Гіббса формування наночасток срібла в водному середовищі різними способами. Досліджено кінетику хімічних перетворень в водних розчинах нітрату срібла в умовах плазмової обробки в газорідинному плазмохімічному реакторі періодичної дії. Наведено криві зміни залежності Ag⁺ від тривалості плазмохімічної обробки розчинів та початкової концентрації іонів срібла

Ключові слова: низькотемпературна плазма, розряд, формування, процес, енергія Гіббса, термодинамічний потенціал, рівняння Нернста, константа швидкості

Произведен термодинамический расчет свободной энергии Гиббса формирования наночастиц серебра в водной среде различными способами. Исследована кинетика химических превращений в водных растворах нитрата серебра в условиях плазменной обработки в газожидкостном плазмохимическом реакторе периодического действия. Приведены кривые изменения зависимости Ag⁺ от продолжительности плазмохимической обработки растворов и начальной концентрации ионов серебра

Ключевые слова: низкотемпературная плазма, разряд, формирование, процесс, энергия Гиббса, термодинамический потенциал, уравнение Нернста, константа скорости

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1. Introduction

Today, plasma discharges of various configurations are finding increasing application in many industries. Therefore, plasmochemical treatment is used in water treatment technologies to change the physicochemical properties, disinfection and purification of water [1]. Plasmochemical treatment of wastewater of various compositions is effective in reducing or completely neutralizing a number of organic and inorganic compounds. Many modifications of polymer surfaces (films) for changing existing and providing new characteristics, processing and bleaching of pulp, etc. are known. Plasma discharges are most often used in nanotechnologies, especially for the preparation of nanoparticles and oxides of various metals [2].

Silver nanoparticles and dispersions are the most popular. Such interest is due to a combination of the pronounced antibacterial effect of silver nanoparticles with the properties typical of nanomaterials. In turn, plasmochemical prepara-tion of silver nanoparticles minimizes the number of reagent components, which expands the practical application of silver nanoparticles even more.

One of the promising directions of practical application of gas-liquid plasmochemical processes for the preparation of silver nanoparticles is the use of contact non-equilibrium low-temperature plasma (CNP) [3]. The plasmochemical method of forming silver nanoparticles is innovative and highly effective in comparison with conventional methods and allows obtaining stable silver nanodispersions. The advantage is also that the process is environmentally friendly and single-stage. In view of this, studies aimed at improving and developing the technology of plasmochemical preparation of silver nanodispersions by varying the plasma parameters affecting the final synthesis product should be considered relevant. The authors' studies of the processes of plasma treatment of solutions of media of various composition show that the properties of synthesized inorganic products depend on a number of factors [3, 4]. Among them,

one can distinguish: the effect of discharge current, reactor pressure, solution concentration, solution temperature and acidity, etc. The phenomenon of nonmonotonic changes in the redox potential of plasmochemically treated solutions with increasing content of silver ions in them is revealed. It is obvious that this pattern may be due to differences in the number of output products of the redox conversion of the main components of H_2O and $AgNO_3$. To confirm these conclusions, detailed studies of thermodynamic and kinetic patterns of plasma treatment of silver nitrate solutions are required.

2. Literature review and problem statement

As is known, thermodynamic calculations allow reducing the volume of pilot studies for determining the technological parameters of the chemical conversion process. In particular, based on thermodynamic calculations, it is possible to investigate the variation patterns of equilibrium composition of the reaction medium, depending on the concentration of silver solutions. The thermodynamic potential of formation of silver nanoparticles $\Delta G^0_{f(AgNPs)}$ in an aqueous medium is one of the key parameters necessary to understand the physicochemical behavior of silver nanoparticles. Data on the calculation of $\Delta G^0_{f(AgNPs)}$ in the aqueous medium are not enough. Moreover, in available publications there are disagreements regarding the calculation of Gibbs free energy in aqueous solutions.

The thermodynamic calculation of the formation of silver nanoparticles in aqueous solutions is made on the basis of an analysis of the calculated values of the Gibbs free energy change (thermodynamic potential) [4, 5]. In this case, the thermodynamic potential $\Delta G^0_{f(AgNPs)}$ and the excess surface energy are considered as a function of the size of silver particles and the average number of atoms (clusters) in each nanoparticle [6, 7]. However, it should be noted that these works consider the size of silver particles of 0.16-10 nm. This means that there are no data on the value of the corresponding indicator for larger nanoparticles. The calculated values obtained by these methods have both positive and negative values. For larger nanoparticles (up to 45 nm), the thermodynamic potential $\Delta G^0_{f(AgNPs)}$ in the aqueous medium is calculated according to the Nernst equation [8]. In this case, experimental data on the shift of the nanosilver electrode potential are used. It is reported that $\Delta G^0_{f(AgNPs)}$ has positive values.

According to the authors [9, 10], it is more expedient to perform the thermodynamics analysis using the equilibrium rate constant of the redox reaction of formation of silver nanoparticles. This takes into account the concentration of silver nanoparticles formed. However, the Gibbs free energy was calculated by this method only for silver particles of 4.5–15.5 nm.

In addition, the above works provide no comparison of the theoretically calculated particle sizes with the particles that are formed under the experimental conditions of different methods of preparation.

The inconsistency of the data indicates that the thermodynamic calculation of the formation of silver nanoparticles requires consideration of many factors, which are generally simplified.

Chemical conversion during the formation of silver nanoparticles in various media has been studied for a long time. In [11–13], kinetic characteristics (rate constants, reaction order) of formation of silver nanoparticles by different methods have been presented. The results obtained differ depending on the conditions of synthesis of silver nanoparticles, but generally agree. The consistency of the data is due to the fact that in all the presented works the preparation of nanoparticles is carried out by one method of chemical reduction.

The formation of nanoparticles under plasma discharge conditions is not typical. The CNP discharge is formed between an electrode in a gas phase and the liquid surface, where the second electrode is located. In the course of such discharge, a significant amount of chemically active particles is formed. It is obvious that the kinetics of chemical conversion (rate constants, distribution curves of the yield of silver nanoparticles formed depending on duration of plasmochemical treatment of solutions) in such a medium differ from the current ones and is more complicated.

In [14], thermodynamic and kinetic data of the formation of hydrogen polyoxide and other reactive compounds formed under the impact of CNP discharge have been given. Mathematical models of kinetic processes of formation of various inorganic compounds in the gas-liquid rector have been investigated in previous publications. In [3, 15], data on the efficiency of preparation of silver nanoparticles by the plasmochemical method without the use of stabilizers and in the presence of sodium alginate in comparison with conventional synthesis methods have been given. The influence of the stabilizer concentration on the yield of silver nanoparticles has been investigated in detail and the characteristics of the particles formed have been given.

Thus, at present there are no theoretical and experimental data on dimensional characteristics of silver nanoparticles in aqueous solutions under plasma discharge conditions. There are also no experimental data on the influence of plasma discharge duration and solution composition (concentration of Ag^+ ions) on the yield and size of silver nanoparticles formed. Therefore, it is of scientific and practical interest to study the thermodynamic and kinetic patterns of formation of silver nanoparticles under plasma discharge impact.

3. The aim and objectives of the study

The aim of the study is the thermodynamics and kinetics analysis of formation of silver nanoparticles in aqueous media under the impact of contact non-equilibrium low-temperature plasma discharge in the gas-liquid reactor. This will allow, firstly, reducing the number of pilot studies to determine the technological parameters of the process of chemical conversion of silver nitrate into silver nanoparticles. Secondly, it will be possible to determine the optimum technological parameters for obtaining the final product of synthesis of silver nanoparticles.

To achieve this aim, the following objectives were accomplished:

– to perform the thermodynamic calculation of formation of silver nanoparticles in the aqueous medium and to compare the calculation data of the most likely sizes of silver nanoparticles with the actually formed as a result of plasmochemical synthesis in the gas-liquid reactor;

– to investigate the kinetics of chemical conversion (reaction rate constant, reaction order) in aqueous solutions of silver nitrate under plasma treatment conditions in the gas-liquid plasmachemical reactor.

4. Materials and methods of the thermodynamics and kinetics analysis of formation of silver nanoparticles

4. 1. Calculation of the Gibbs free energy of formation of silver nanoparticles in aqueous solutions

The standard Gibbs free energy of formation of silver nanoparticles was calculated in three ways:

1. According to the Thomson-Gibbs equation for spherical particles [6, 7]:

$$\Delta G^0_{f(AgNPs)} = \frac{2\sigma_{Ag}M_{Ag}}{\rho_{Ag}r_{AgNPs}} = \frac{23.45\,\text{kJ} \cdot \text{nm} \cdot \text{mol}^{-1}}{r_{AgNPs}}, \qquad (1)$$

where σ_{Ag} is the coefficient of surface tension of silver, N/m; M_{Ag} is the atomic weight of silver, $108.0 \cdot 10^{-3}$ kg/mol; ρ_{Ag} is the density of silver, $10.5 \cdot 10^6$ g/m^3 [16]; r_{Ag} is the radius of silver nanoparticles, nm.

2. According to the Nernst equation [8]:

$$\Delta G^0_{f(AgNPs)} = -Z \cdot F \cdot E + 77.120, \qquad (2)$$

where Z is the number of electrons; F is the Faraday constant, 96485.55 Cl/mol; E is the electrode potential, B [4]; 77.120 is the standard Gibbs free energy of Ag^+_{aq} formation, kJ/mole.

3. Using the equilibrium constant of the corresponding redox reactions [9]:

$$\Delta G_r = -R \cdot T \cdot \ln K, \qquad (3)$$

$$K = \frac{\left[Ag^+_{(aq)}\right]}{\left[H^+_{(aq)}\right]\left[O_{2(aq)}\right]^{1/4} C^\theta_{AgNPs(E)}}, \qquad (4)$$

where ΔG_r is the Gibbs free energy, which changes the redox reaction, J/mol; R is the universal gas constant, 8.314 J/K·mole; T is the absolute temperature, K; K is the equilibrium constant; $C_{AgNPs(E)}$ is the equilibrium concentration of nanosilver, mol/l; [H^+_{aq}] is the equilibrium concentration of H$^+$ protons, mol/l; [$O_{2(aq)}$] is the equilibrium concentration of O$_2$, mol/l; [Ag^+_{aq}] is the equilibrium concentration of Ag$^+$, mol/l; θ is the coefficient associated with the nanosilver properties, (0–1) [17].

4. 2. Kinetic studies of formation of silver nanoparticles by the plasmochemical method

The study was performed in a model plasmachemical reactor, which is described in detail in previous papers [3, 14]. To produce a plasma discharge, the reactor pressure was reduced by $9 \cdot 10^3$ Pa, and voltage of 550–600 V was applied to the electrodes. The current strength in the circuit was 120 mA. The distance from the anode to the solution surface was maintained at 1 cm.

The solutions were prepared by silver nitrate dissolution in bidistilled water in a given ratio.

To characterize silver nanoparticles formed, the reaction mixture was analyzed using a spectrophotometer. The spectra of colloidal solutions were obtained on a UV-5800PC spectrophotometer using quartz cells in the wavelength range of 300–700 nm.

Particle size distribution and average size were measured using the Zetasizer Nano-25 particle size analyzer (England).

The pH of initial solutions and prepared dispersions was measured using a pH-150 MI meter (relative measurement error of 0.5 %).

5. Results of studies of kinetics and thermodynamics of plasmochemical formation of silver nanoparticles

For comparison, the standard Gibbs free energy of formation of silver nanoparticles was calculated in three different ways. The values of the calculation of the Gibbs free energy of formation of silver nanoparticles in aqueous media using the Thomson-Gibbs (1), Nernst (2) equations and equilibrium constants of the corresponding redox reactions (3) are presented in Fig. 1.

The data obtained confirm the discrepancy of the data available in the literature, and the Gibbs free energy of formation of nanoparticles, depending on the size, may have either a positive or a negative value. However, the data obtained show a general pattern: the Gibbs free energy of formation of nanoparticles in aqueous solutions increases with decreasing size of silver particles. The data in Fig. 1 are theoretically calculated and therefore determine only the thermodynamic probability of forming nanoparticles of different sizes according to the accepted conditions (temperature, particle shape, etc.).
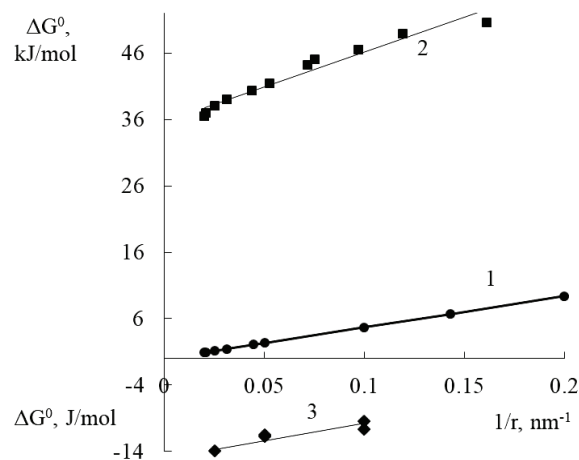
Fig. 1. Dependence of the standard Gibbs free energy ($\Delta G^0_{f(AgNPs)}$) of formation of silver nanoparticles on the particle radius (r_{AgNPs}) calculated in various ways

The size of the particles actually formed in the aqueous solution under plasma discharge conditions was determined. To do this, the study of particle size distribution was performed, and the average particle size (Table 1) of plasmochemically prepared silver dispersions at different initial concentrations of Ag$^+$ was determined. As a result of the plasmochemical impact, silver nanoparticles with a wide size distribution (5–120 nm) are formed. Thus, the experimental data are consistent with the estimated, but both small (5–50 nm) and much larger silver particles are actually formed. The data obtained (Table 1) indicate that the average diameter of the nanoparticles formed under plasma discharge impact is 36.5–60.1 nm and increases with increasing initial concentration of Ag$^+$.

It is known that the study of kinetic patterns of chemical processes involves determining the dependence of the process rate on the main technological parameters: concentration of reagents and influence of external factors (temperature, mixing intensity, etc.). We consider mixing temperature and intensity to be constant values, since

during the plasmochemical treatment at a given current, the intensity of hydrogen release at the cathode causes uniform mixing of the system.

Table 1

Size of silver nanoparticles prepared in plasma treatment conditions (experimental data)

C Ag$^+$, mmol/l	d_{AgNPs}, nm
0.25	36.5±1.2
0.5	38.0±2.3
0.7	40.2±1.6
1.0	50.1±2.7
3.0	60.1±2.0

The dependence of the equilibrium concentration of silver ions on duration of plasma discharge impact at different initial concentrations of silver ions in the solution is investigated. The data are shown in Fig. 2.
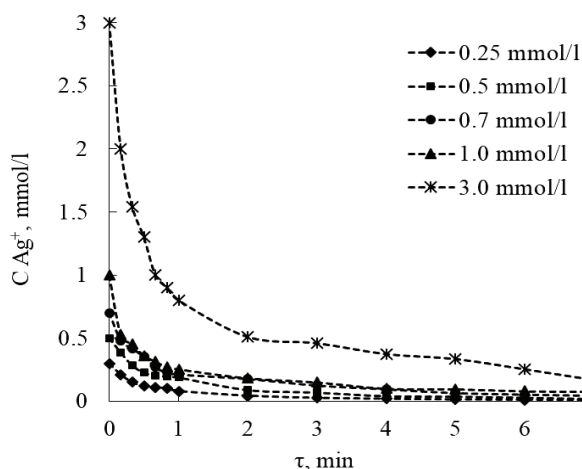

Fig. 2. Dependence of Ag$^+$ concentration on duration of plasma discharge impact at different initial concentrations of silver ions in the solution (the curves are not an approximation and are given to visualize the dependence on a qualitative level)

For all investigated initial Ag$^+$ concentrations, a decrease in Ag$^+$ concentration with increasing treatment time up to 7 min is observed. In this case, the conversion of Ag$^+$ to Ag^0 for all investigated concentrations by more than 50–80 % occurs after 1–2 min of plasma discharge impact. The formation of silver nanoparticles is confirmed by the experimentally determined spectra of the prepared dispersions of silver nanoparticles and the SPR absorption maximum (λ_{max}) at 400–440 nm (Fig. 3).

According to the experimental data (Fig. 3), the values of the rate constants of plasmochemical formation of silver nanoparticles were calculated (Table 2).

The data obtained suggest that the process of plasmochemical formation of silver nanoparticles is the second-order reaction and is characteristic of formation of silver nanoparticles using different types of reducing agents [13].

The influence of CNP duration on pH of silver nitrate solutions of different concentrations is investigated (Fig. 4).

The data obtained suggest that the CNP discharge treatment of solutions provides a decrease in pH from 7.0–7.27 to 2.6–2.9 at the investigated initial concentrations of silver ions. The intense reduction of the solution acidity is likely to be due to the consumption of OH radicals to form hydrogen polyoxides and transfer of electrons of H radicals to the solution. After the rapid decrease in pH to 3.4–3.7, the pH value is stabilized and maintained. It should be noted that H radicals are the main reducing agents in this case.
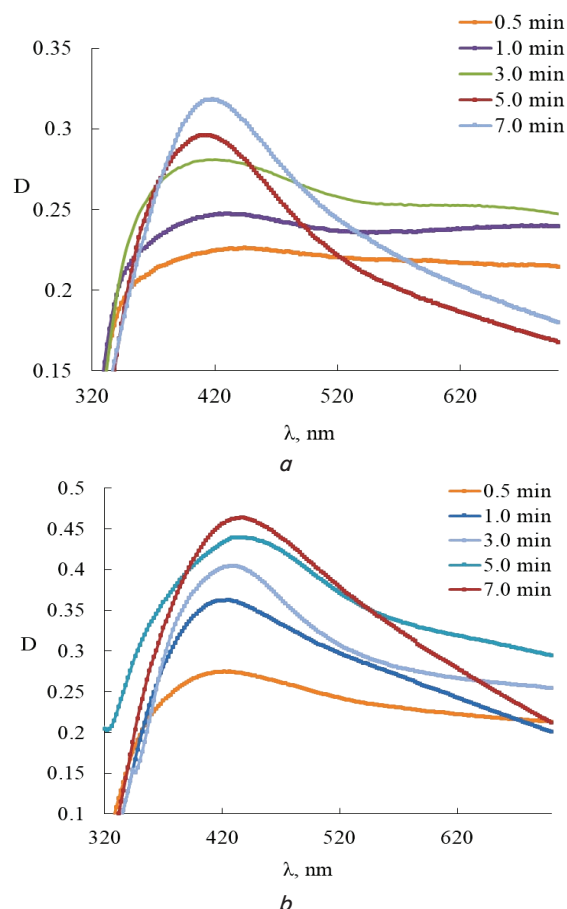

Fig. 3. Dependence of absorption spectra of plasmochemically prepared dispersions of silver nanoparticles on plasma treatment duration at different initial Ag concentrations: a — Ag$^+$ 0.001 mol/l, b — Ag$^+$ 0.003 mol/l ($I = 120$ mA, $P = 0.08$ MPa)

Table 2

Values of rate constants of plasmochemical formation of silver nanoparticles

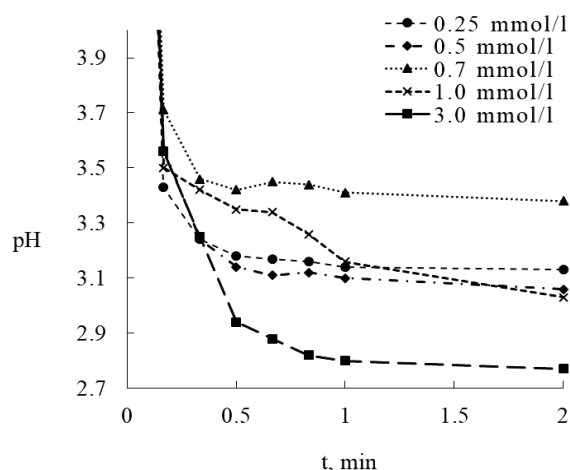| C Ag$^+$, mmol/l	k, mol^{-1}·dm^3·min^{-1}
0.25	1.53 ($R=0.98$)
0.5	0.60 ($R=0.95$)
0.7	0.28 ($R=0.98$)
1.0	0.17 ($R=0.98$)
3.0	0.076 ($R=0.93$)

Fig. 4. Dependence of pH of silver nitrate solutions of different concentrations on plasma treatment duration

6. Discussion of results of the study of the thermodynamics and kinetics analysis of formation of silver nanoparticles

The divergence of the data of thermodynamic calculations obtained in different ways is quite predictable. The matter is that in different equations used for calculation, different parameters were taken into account. The difference between the calculation data and sizes of silver particles actually formed is also expected. This can be explained by the fact that assumptions about an ideal spherical shape of nanosilver are used in calculations. While actually silver nanoparticles (AgNPs) have particles of different shapes [12].

In addition, the shape or morphology of nanosilver (as well as the crystalline structure) has a significant influence on its thermodynamic properties. As a rule, nanoparticles are considered as ideal spheres, while in fact it is not [8]. Thus, the above factors determine the difference of the calculation data of thermodynamic formation of silver nanoparticles.

It is well known that the nature of the reducing agent (reduction potential, E_0) is an important factor that controls the size, shape and size distribution of silver nanoparticles [16, 18]. Under the CNP impact on aqueous media, rather stable non-radical particles, such as products of oxidation and reduction of water molecules, should be considered as the main reactive components. The concentration of these compounds in the reaction medium varies with the prolongation of plasma impact. However, it is similar under the studied conditions (current strength, pressure, treatment time) with increasing initial content of silver ions. Taking into account the above, the reduction of the process rate constant with increasing content of silver ions is quite natural (Table 2).

As is known from [14], the change in the acidity of aqueous solutions in the course of CNP treatment is due to the cathode process of water allocation on the surface of the electrode immersed in the solution and the anode process of water oxidation on the surface of the solution in the CNP impact zone:

$$2H_2O + 2e \rightarrow H_2 + 2OH^-, \tag{5}$$

$$2H_2O - 4e \rightarrow O_2 + 4H^+. \tag{6}$$

It is also known that the pH of distilled water in plasmochemical treatment is rapidly reduced to 2–3 units. Such acidification of distilled water in the course of CNP impact is due to accumulation of hydrogen polyoxides in the solution, which are characterized by strong acid properties [14]. Thus, the decrease in the solution acidity (Fig. 5) is due to the consumption of OH radicals to form hydrogen polyoxides.

In the paper, thermodynamic calculations are given, and kinetic characteristics of formation of silver nanoparticles under plasma discharge impact are determined. However, for widespread practical application, it is expedient to obtain silver nanoparticles in the presence of stabilizers of different origin. It would be advisable to determine the appropriate characteristics in the presence of different stabilizers.

7. Conclusions

1. The thermodynamics analysis of formation of silver nanoparticles in aqueous solutions using various methods for calculating the Gibbs free energy is carried out. Depending on the method of calculation of $\Delta G^0_{f(AgNPs)}$, it is from −9.43 to −14.48 J/mol and 36.5–50.6 KJ/mol. The pattern is revealed: the Gibbs free energy in aqueous solutions increases with decreasing size of silver particles. Comparison of the calculation data of silver nanoparticles formed is consistent with the actually formed as a result of plasmochemical synthesis. In the experiment, the size of the formed particles has a wide range of values. Based on experimental data, the average particle size depending on the initial concentration of silver ions in the solution is determined.

2. The kinetics of chemical conversion in aqueous solutions during plasmochemical treatment of aqueous solutions of silver nitrate are investigated. It is found that the process of plasmochemical formation of silver nanoparticles is the second-order reaction. The rate constant of formation of silver nanoparticles is within $k = 0.076$–1.53 $mol^{-1} \cdot dm^3 \cdot min^{-1}$ depending on the initial concentration of silver ions. The formation of silver nanodispersions under plasma discharge impact is characterized by the presence of the peak $\lambda_{max} = 400$–440 nm.

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