

THE INFLUENCE OF STERIC STABILIZATION ON PROCESS OF Au, Pt NANOPARTICLES FORMATION

Nanoparticles are very fascinating area of science not only due to their unique properties but also possibility of producing new more complex materials, which may find an application in modern chemistry, engineering and medicine. In process of nanoparticles formation very important aspect is a rate of individual stage i.e. reduction, nucleation and autocatalytic growth, because this knowledge allows for proper materials design, morphology manipulation, stability. The last one aspect can be realized using proper electrostatic, steric and electrosteric stabilization. However until now nobody reports and measures kinetic rates of all stages during process of particles formation in the presence of steric stabilizers. Thus, the main contribution of this paper is determination of individual rate constants for nanoparticles formation in the presence of steric stabilizers and their comparison to the system without stabilizer. For this purpose, an aqueous solution of Au(III) and Pt(IV) ions were mixed with steric stabilizers like PVA and PVP, and reduced using L-ascorbic acid as a mild and sodium borohydride as a strong reductant. As a results stable nanoparticles were formed and process of their formation was registered spectrophotometrically. From obtained kinetic curves the values of observed rate constants for reduction metal ions, slow nucleation and fast autocatalytic growth were determined using Watzky-Finke model. It was found that the addition of polymer affects the rate of the individual stages. The addition of steric stabilizers to gold ions reduced with L-ascorbic acid causes that the process of nucleation and autocatalytic growth slows down and the value of observed rate constants for nucleation changes from $3.79 \cdot 10^{-3}$ (without polymer) to $7.15 \cdot 10^{-5} \text{s}^{-1}$ (with PVA) and for growth changes from $1.15 \cdot 10^3$ (without polymer) to $0.48 \cdot 10^2 \text{s}^{-1} \text{M}^{-1}$ (with PVA). However, the rate of the reduction reaction of Au(III) ions is practically unchanged. In case of using strong reductant the addition of polymer effects on the shape of kinetic curve for reduction of Au(III) and it suggests that mechanism is changed. In case of Pt(IV) ions reduction with L-ascorbic acid, the process speeds up a little when PVA was added. Determined values of observed rate constants for nucleation and growth platinum nanoparticles decrease twice comparing to the system without polymer. The reduction of Pt(IV) ions with sodium borohydride accelerates when PVP was added and slows down when PVA was used. Moreover, the size of obtained colloidal gold and platinum was also analysed using DLS method. Obtained results (rate constants) may be useful in the process of nanomaterials synthesis, in particular in microflow.

Keywords: gold, platinum, nanoparticles, kinetic, nucleation growth, steric stabilization

1. Introduction

Metal nanoparticles are known from ancient times but only a few decades ago became one of the most studied objects. This interest results from their unique physicochemical properties which are quite different from their counterpart in the bulk material [1]. Development of research methods allows now for their detailed analysis. Thus, it is not surprising, that they found an application in all areas of our life, and the number of published papers on this subject only in this year reached over 24 500 (Scopus). In the literature the synthesis of particles with different size [2,3] and shape [4,5], surface modification [6], an application in chemistry [7,8], engineering [9], medicine [10-14] are studied extensively. Less papers can be found about kinetic study of nucleation and growth of metal nanoparticles [15-19]. However, a great progress in this field followed the publication of Watzke and Finke [20] and their proposed mathematical model,

which describes slow nucleation and fast autocatalytic growth [15]. Another interesting aspect in the process of nanoparticles formation is their stability [21]. The stability of colloidal particles is determined by the Brownian motion and an interaction between particles during a collision. Usually, there are attractive and repulsive forces. The main source of attraction are Van der Waals-London forces, which cause coalescence of particles of similar composition. For many colloidal systems, the range of interaction of Van der Waals-London forces is within the range 5-10 nm and only appropriate repelling forces can counteract the attraction of particles and their stabilization. The repulsive forces should be at least as strong as the attractive forces and comparable in the range of the attractive interaction. Hence, stability of dispersed particles can be realized by: an electrostatic (charge stabilization), steric and electrosteric stabilization. First one, can be realized by surrounding colloidal particles with an electrical double layer, second one by adsorption or chemisorption of

* AGH UNIVERSITY OF SCIENCE AND TECHNOLOGY, FACULTY OF NON-FERROUS METALS, LABORATORY OF PHYSICAL CHEMISTRY AND ELECTROCHEMISTRY, AL. A. MICKIEWICZA 30, 30-059 KRAKOW, POLAND

Corresponding author: mlb@agh.edu.pl

polymeric molecules and last one is a combination of the two previous. The electrostatic stabilization works only in polar liquid and is very sensitive to ionic strength. This stabilization is most effective for media with low value of ionic strength $I \leq 1$ mM. The increase of ionic strength causes decreasing of double layer thickness and in consequence particles coagulation. However, charge stabilization is still widely used due to its simplicity and price. In opposite to electrostatic stabilization is steric stabilization, which is realized by a polymer addition to the colloidal solution. The chain dimensions of polymers with molecular weight above 10 kD are comparable or in excess to the range of Van der Waals-London interaction and provide good stabilization even in the system with high value of ionic strength. Steric stabilization of particles in the solution is achieved by attaching of polymer molecules to the particles surface and layer formation. Steric stabilization has several advantages in comparison to electrostatic stabilization like: insensitivity to ionic strength, comparable efficiency in aqueous and nonaqueous media, it works similarly in solutions with low and high concentration of particles, reversibility of flocculation. Thus, steric stabilization is more effective and flexible method of particles stabilizations. During nanoparticles synthesis via chemical route, a polymer is usually added to metal precursor or reductant as sufficient stabilizing agent. After that, reagents are mixed together and process of nanoparticles formation begins. However until now nobody reports and measures kinetic rates of all stages during process of particles formation in the presence of steric stabilizers. Thus, the main contribution of this paper is determination of individual rate constants for nanoparticles formation in the presence of steric stabilizers and their comparison to the system without stabilizer. For this purpose, an aqueous solution of Au(III) and Pt(IV) ions were mixed with steric stabilizers like polyvinyl alcohol (PVA) and polyvinylpyrrolidone (PVP), and reduced using L-ascorbic acid as a mild and sodium borohydride as a strong reductant. As a results stable gold and platinum nanoparticles were formed and process of their formation was registered spectrophotometrically. From obtained kinetic curves the values of observed rate constants for reduction metal ions, slow nucleation and fast autocatalytic growth were determined using Watzky-Finke model.

2. Materials and methods

2.1. Chemicals

Gold precursor. As a precursor of metallic gold, an aqueous solution of HAuCl_4 was used. 0.1M base solution was prepared by dissolving pure Au (99.99% purity, obtained from Mennica Państwowa, Warsaw, Poland) in aqua regia. After several evaporations of this solution and dilution of the obtained solid in deionized water, the starting substrate was obtained, which was next dissolved in hydrochloric acid. Before each experiment, the fresh solutions of Au(III) were prepared. For this purpose the proper volume of base solution of gold ions was diluted in 0.1 M HCl.

Platinum precursor. The base solution of platinum precursor, i.e. 0.076M solution of H_2PtCl_6 was obtained from metallic platinum with purity 99.99% (Mennica Państwowa, Warsaw, Poland). For this purpose the metallic platinum was dissolved in aqua regia solution which was dried several times to remove an excess of nitric acid and at the end in hydrochloride acid to keep the acidic pH of base solution. Before each experiments the fresh solution of Pt(IV) ions was prepared, then the proper volume of base solution was diluted in deionized water.

Reductant. The base solution of L-ascorbic acid (H_2Asc , Sigma-Aldrich, Germany) was prepared via dissolving in deionized water a proper amount of powder. Sodium borohydride (p.a., Fluka) was dissolved in 0.06 M or in 0. M NaOH (p.a., POCH, Poland) in order to prevent its decomposition.

Stabilizers. As a stabilizer, polyvinyl alcohol and polyvinylpyrrolidone were used. Aqueous solutions of PVA (p.a., M_w 67,000 g/mol, Sigma Aldrich, Germany) and PVP (p.a., M_w 10,000 g/mol, Sigma Aldrich, Germany) were prepared in such a way, that 0.5 g of powder was dissolved in 50 mL of deionized water. Dissolution of PVA was enhanced via ultrasounds and heating up to 40°C. The proper volume of PVA and PVP was added to the metal precursor.

2.2. Methods of analysis

In conducted experiments the reduction of metal complex ions with proper reductant was monitored at fixed wavelength i.e. 314 nm for Au(III) and 262 nm or 360 nm for Pt(IV) ions using spectrophotometer Stopped Flow (Applied Photophysics, UK) working in the UV-vis range (from 190-900 nm wavelength) with the 1-cm optical path. The same spectrophotometer was used for nucleation and autocatalytic growth registration.

The size and size distribution of obtained particles were analyzed using dynamic light scattering (DLS) method. For this purpose, directly after kinetic curve registration, the solution with colloidal gold and platinum was analyzed using Nanozetasizer Nano-ZS (Malvern, UK).

3. Results

3.1. Experimental conditions

The process of Au(III) and Pt(IV) reduction with ascorbic acid and sodium borohydride as well as nucleation and autocatalytic growth were conducted under selected conditions gathered in Table 1.

The process of nanoparticles formation was registered in the solution without and with polymer addition. The choice of applied amount of stabilizer was made experimentally. Tests confirmed that the choice of mass ratio of the polymer to metal ions equal to 10:1 is optimal. In case when $m_{\text{polymer}}/m_{\text{metal}} = 1$, obtained particles form aggregates one week after synthesis. When $m_{\text{polymer}}/m_{\text{metal}} = 100$ the gold particles were stabilized at

TABLE 1

Conditions applied for kinetic measurements of redox reaction, nucleation and growth of platinum nanoparticles in results of reaction between metal chloride complex ions and reductant.

Initial concentration of Au(III) ions was fixed at 0.15 mM and for Pt(IV) at 1.00 mM (reaction with ascorbic acid) and 0.05 mM (with sodium borohydride).

Each experiment was repeated 6 times

Reductant	Initial concentration of reductant, mM	Mass ratio of polymer to metal complex	T, K	pH	[Cl] ⁻ , M
Au nanoparticles					
H ₂ Asc	3.0	10:1	298	1.33	0.05
NaBH ₄	0.3			4.0	
Pt nanoparticles					
H ₂ Asc	60	10:1	313	2.5	0.00
NaBH ₄	3.0		298	12	

the same level as in case of much lower excess of polymer. In case of platinum nanoparticles, the addition of polymer at a mass ratio $m_{polymer}/m_{metal} = 50$ causes rapid aggregates formation, due to polymer flocculation.

3.2. Spectra of reagents

The aqueous solution of Au(III) complex ions shows strong absorption band with maximum at the wavelength $\lambda = 314$ nm [22]. This value corresponds well to that known from the literature [23] and confirms the presence of $[AuCl_4]^-$ complex ions in the studied system. The aqueous solution of Pt(IV) complex ions also shows characteristic spectrum with maximum at 200, 262, 455 nm and the edge of the spectrum at 360 nm (Fig. 1). The intensity of each spectra according to Lambert-Beer law strongly depends on metal ions concentration. It is known, that ascorbic acid also has a characteristic spectrum with maximum at 246 nm [22].

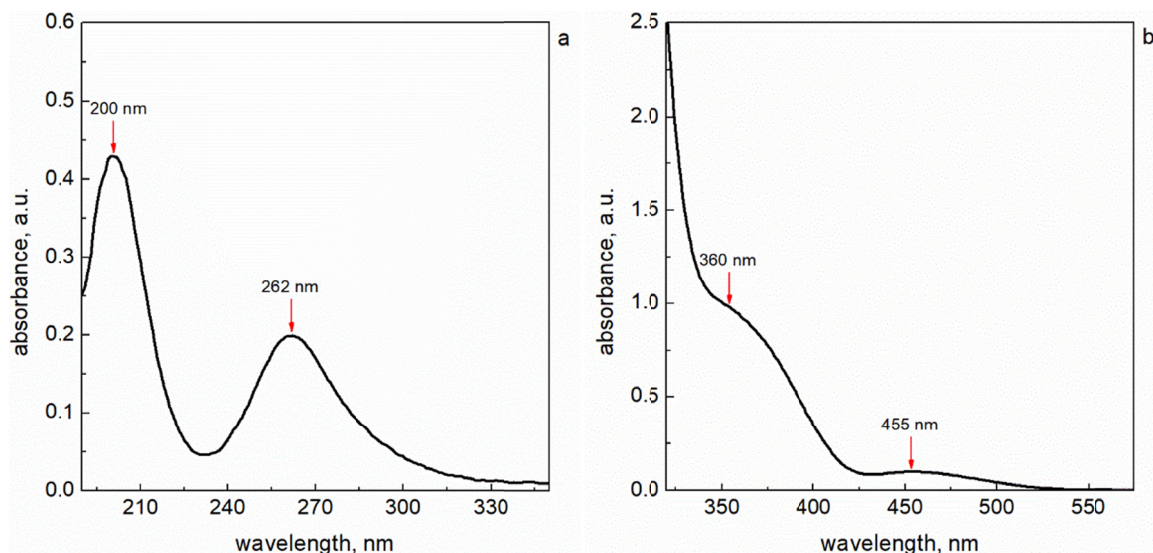
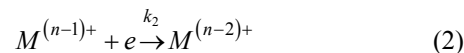
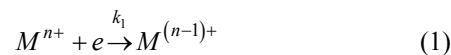


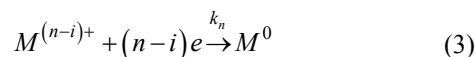
Fig. 1. Spectra of aqueous solution of Pt(IV) ions. Conditions: $C_0, Pt(IV) = 0.1$ mM (a); $C_0, Pt(IV) = 2.0$ mM (b), $T = 20^\circ C$, path length 1 cm

3.3. Kinetic study

The first step in the process of nanoparticles formation is a reduction reaction between metal ions and selected reductant. Depending on the oxidation state of metal precursor and type of the reductant, reduction reaction may proceed as the subsequent reaction which can be expressed as follows:

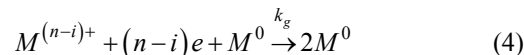


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In this scheme M^{n+} denotes metal on “n” oxidation state and M^0 – metal on zero oxidation state, $k_{1,2,\dots,n}$ denote corresponding rate constants.

The reaction (3) is the last step in reduction process and describes nucleation process. In this work, it is shown as a second stage in the process of nanoparticles formation. During nucleation process, metal precursor is reduced to zero oxidation state i.e. the first metallic atoms are formed. Next, atoms form more stable cluster. After that, the autocatalytic process takes place in which clusters grow and nanoparticles are formed. The autocatalytic growth can be expressed as:



where k_g denotes rate constant for growth process.

The reactions and result from Watzky-Finke model, for which a differential equation describing nucleation and growth has the following form:

$$\frac{dC_{M^0}}{dt} = k_n C_{M^{(n-i)+}} + k_g C_{M^{(n-i)+}} C_{M^0} \quad (5)$$

In practice, under isolation conditions (high excess of reductant in comparison to metal ions), the values of rate constants

are in fact observed rate constants $k_{n,obs}$ and $k_{g,obs}$ for nucleation and growth $k_{n,obs} = k_n C_R$, $k_{g,obs} = k_g C_R$, where C_R – reductant concentration. It simplifies equation yielding:

$$\frac{dC_{M^0}}{dt} = k_{n,obs} C_{M^{(n-1)+}} + k_{g,obs} C_{M^{(n-1)+}} C_{M^0} \quad (6)$$

Depending on the number of steps taking place before reaction during reduction process, the equation describing initial concentration of $M^{(n-1)+}$ can be proposed based on kinetic study or by the examination of the kinetics of previous steps. For example, it was shown in previous study [22] that reduction reaction of Au(III) ions with ascorbic acid is two-stage process. In first step, reduction of Au(III) to Au(I) takes place and the change of Au(III) concentration in time can be expressed as:

$$C_{Au(III)} = C_{0,Au(III)} \exp(-k_{1,obs} t) \quad (7)$$

where observed rate constant ($k_{1,obs}$) is described by the following equation: $k_{1,obs} = k_1 C_{H_2Asc} = 44 \cdot 10^7 \exp(-5005T^{-1})$ and k_1 – first-order rate constant, $C_{0,Au(III)}$, $C_{Au(III)}$ denote initial concentration of gold ions and concentration at the “ t ” time, respectively.

Based on equation and the mass balance between Au(III) and Au(I):

$$C_{0,Au(I)} = C_{0,Au(III)} - C_{Au(III)} \quad (8)$$

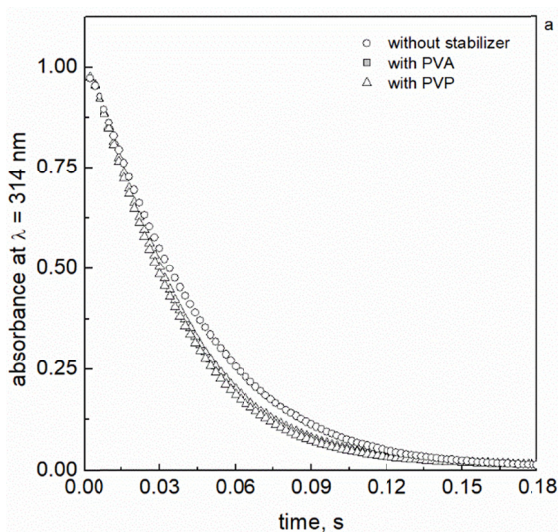
it is possible to determine initial concentration of Au(I), whose disappearance cannot be observed spectrophotometrically:

$$C_{0,Au(I)} = C_{0,Au(III)} (1 - \exp(-k_{1,obs} t_i)) \quad (9)$$

where: t_i – incubation time, $C_{0,Au(I)}$ – initial concentration of Au(I) ions.

After integration, the equation has following form:

$$\ln \frac{C_{Au}}{C_{0,Au(III)} - C_{Au}} = \ln \frac{k_{n,obs}}{k_{g,obs} C_{0,Au(III)}} + (k_{n,obs} + k_{g,obs} C_{0,Au(III)}) t \quad (10)$$



Using eq. (10) the value of observed rate constant for the nucleation and growth process can be determined from the slope and the intercept of its graphical form.

3.3.1. Gold nanoparticles formation

Using spectrophotometer, the process of reduction of metal ions and nanoparticles formation was registered and obtained curves for Au(III) ions with L-ascorbic acid and nucleation and growth using different stabilizer are shown in Fig. 2.

Presented kinetic curves shown in Fig. 2a look similar. It suggests, that addition of polymer does not affect the rate of reduction reaction of Au(III) ions. Taking into account these results, and making the assumption that the stabilizer does not affect the reductant in considered time it was possible to determine the values of rate constants (Table 2) for the first stage of the process of nanoparticles formation based on obtained kinetic curves (Fig. 2a).

TABLE 2

Observed rate constants for reduction reaction of Au(III) ions with L-ascorbic with and without stabilizer. Conditions: $C_{0,Au(III)} = 0.15$ mM, $C_{0,H_2Asc} = 3.0$ mM, $T = 298$ K, $m_{polymer} : m_{Au(III)} = 10 : 1$

Polymer	$k_{1,obs} \pm \sigma, s^{-1}$	$k_1 \cdot 10^{-3} \pm \sigma, M^{-1}s^{-1}$	R^2
Without	22.99 ± 0.24	7.67 ± 0.08	0.998
PVA	27.27 ± 0.33	9.09 ± 0.11	0.997
PVP	28.46 ± 0.33	9.48 ± 0.11	0.997

In the next stage, the reduction of Au(I) to Au(0) takes place. Unfortunately, due to the absence of the spectrum characteristic for the gold (I) complex, it is not possible to follow the Au(I) ion reduction reaction to Au(0), and thus to describe its corresponding kinetic equation. The subsequent steps, i.e.: nucleation and particle growth can be recorded spectrophotometrically by

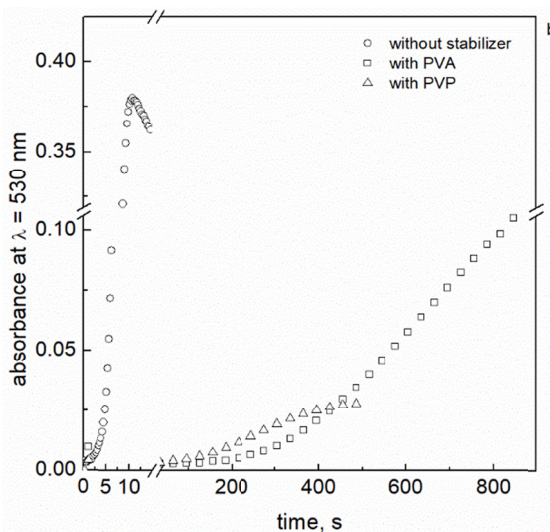


Fig. 2. Kinetic curve for reduction reaction of Au(III) ions with L-ascorbic acid (a) nucleation and growth (b) without and with PVA and PVP additions. Conditions: $C_{0,Au(III)} = 0.15$ mM, $C_{0,H_2Asc} = 3.0$ mM, $pH = 1.33 \pm 0.05$, $T = 298 \pm 0.1$ K, $m_{polymer} : m_{Au(III)} = 10 : 1$

monitoring the level of turbidity of the solution in the visible spectrum. Usually kinetic curve is registered at the wavelength for which the maximum absorbance value is recorded on the plasmon. The sample of kinetic curve of reduction of Au(III) to Au(I) and sigmoidal character of the curve describing slow nucleation and fast autocatalytic growth is shown in Fig. 3. In the inset, nucleation zone is shown in red.

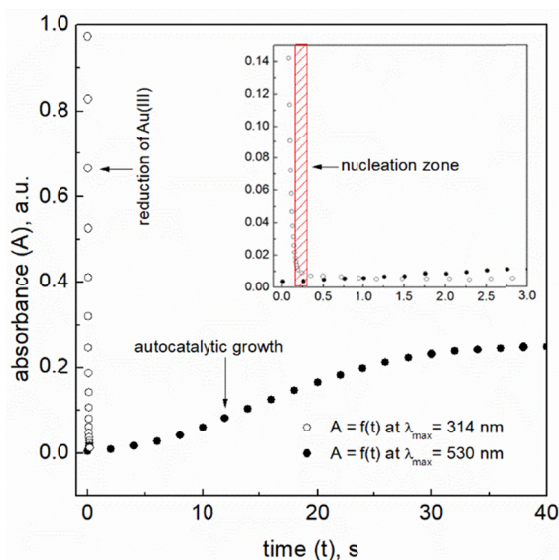


Fig. 3. Kinetic curve for reduction reaction of Au(III) ions with L-ascorbic acid, nucleation and growth without polymer. Conditions: $C_{0,Au(III)} = 0.15$ mM, $C_{0,H_2Asc} = 3.0$ mM, $pH = 1.33 \pm 0.05$, $T = 298 \pm 0.1$ K

As a result, at the selected wavelength (i.e. 530 nm) we obtain a curve for the solid phase precipitation process responsible for the Au(0) transition to the colloidal gold. Due to the fact that it is difficult to determine the exact moment of the nucleation process on the precipitation curve (Fig. 3), and thus to determine the rate constants, Watzky-Finke model was applied. Based on this model, the nucleation and growth process

of gold nanoparticles can be described in two steps as reduction Au(I) to Au(0) according to nucleation and autocatalytic growth (sigmoid character on the curve, e.g. Figure 2b). Depending on the polymer addition, the process of nucleation and growth takes more time. The induction time of this process is prolonged, which may indicate the presence of diffusion in the reacting system. The values of observed rate constants for nucleation and autocatalytic process were determined from graphical form of equation (10) and are gathered in Table 3.

TABLE 3

The value of observed rate constants for nucleation and growth of gold nanoparticles obtained as a results reduction reaction between Au(III) ions and ascorbic acid. Conditions: $C_{0,Au(III)} = 0.15$ mM, $C_{0,H_2Asc} = 3.0$ mM, $T = 298$ K, $m_{polymer} : m_{Au(III)} = 10 : 1$

Polymer	t_i , s	$(k_{n,obs} \pm \sigma) \cdot 10^3$, s^{-1}	$k_n \pm \sigma$, $M^{-1}s^{-1}$	$k_{g,obs} \pm \sigma$, $M^{-1}s^{-1}$	R^2
Without	1.0	3.79 ± 0.11	1.26 ± 0.03	$1.15 \cdot 10^3$	0.999
PVA	200	$7.15 \cdot 10^{-2} \pm 0.33$	0.02 ± 0.11	48.04	0.997
PVP	180	0.70 ± 0.04	0.23 ± 0.01	74.71	0.995

On the basis of the obtained results, it can be concluded that the nucleation process, and hence the growth rate, is the slowest when adding PVA. This is due to the length of the polymer chain, which is longer for PVA than for PVP. Moreover, the addition of polymers affects the diffusion of atoms, which are produced during redox reaction and significantly slows down the process of clusters formation.

Considering the reduction of Au(III) with sodium borohydride, it can be seen that the process is very rapid and the first stage in reduction process takes only about 5 ms (Fig. 4a) in the absence of stabilizer. For comparison, analogous kinetic measurements were made when a stabilizer was present in the reacting solution. It was found that when to the reacting system PVA or PVP were added the process of reduction slows down

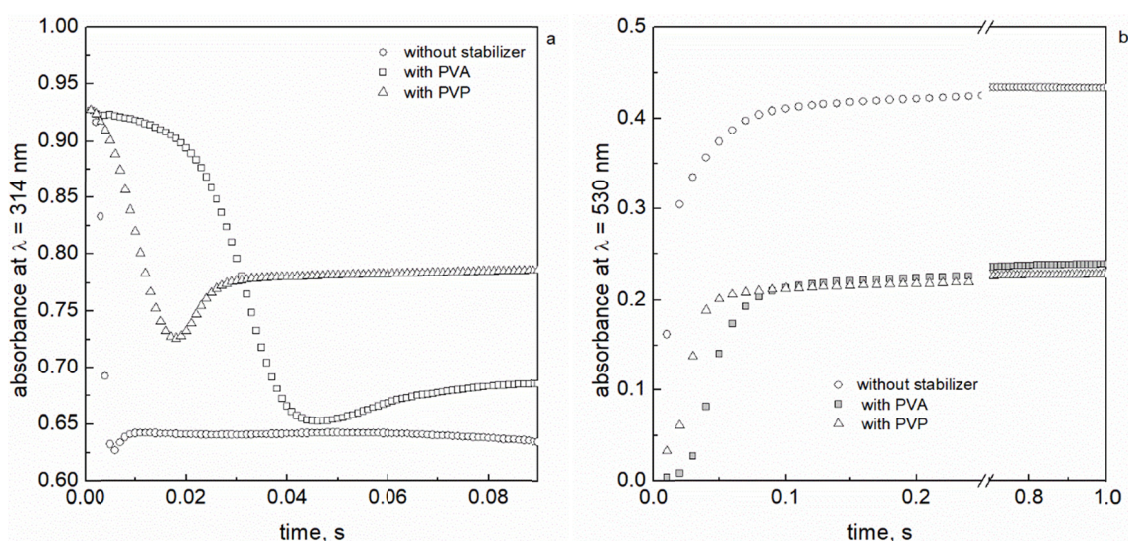


Fig. 4. Kinetic curve for reduction reaction of Au(III) ions with sodium borohydride (a) nucleation and growth (b) without and with PVA and PVP additions. Conditions: $C_{0,Au(III)} = 0.15$ mM, $C_{0,NaBH_4} = 0.3$ mM, $T = 298$ K, $m_{polymer} : m_{Au(III)} = 10 : 1$

and takes about 40 or 20 ms, respectively. Moreover, the shape of kinetic curves is quite different that obtained previously (without stabilizer). It suggests that polymers interact somehow with the reductant or metal ions, especially in case of PVA. Based on the obtained kinetic curves, it was not possible to determine rate constants. Other interesting thing is that the process of nucleation starts earlier than in case of nanoparticles synthesis with L-ascorbic acid. On the kinetic curve, after a few ms a decrease of absorbance at 314 nm from 0.92 up to 0.62 (without stabilizer), 0.72 (with PVP) and 0.65 (with PVA) was observed. After reaching these absorbance level, the sharp increase of absorbance value was observed, which suggests the presence of metallic gold. Fig. 4a shows that the value of absorbance does not reach the level close to zero as it was in case when ascorbic acid was used. It suggests that process of reduction is more complex.

Considering the suggestion of the autocatalytic nature of the reaction as well as the assumption that the Au(I) reduction rate to Au(0) is smaller than Au(III) reduction rate to Au (I), the Watzky-Finke model was used as a model for describing the mechanism of solid gold precipitation (Fig. 4b). It is assumed that the initial concentration of Au(I) ions in the system is equal to the initial concentration of Au(III) ions. The obtained values of rate constants of the nucleation and growth process, determined from the slope and intercept eq. (10) are given in Table 4.

TABLE 4

Observed rate constants for nucleation and growth of gold nanoparticles as a results of Au(III) ions reduction with sodium borohydride (with and without stabilizer). Conditions:

$$C_{0,Au(III)} = 0.15 \text{ mM}, C_{0,NaBH_4} = 0.3 \text{ mM}, T = 298\text{K}, \\ m_{polymer} : m_{Au(III)} = 10 : 1$$

Polymer	$k_{n,obs} \pm \sigma, M^{-1}s^{-1}$	$k_{g,obs} \pm \sigma, M^{-2}s^{-1}$	R^2
without	6.46 ± 0.15	$5.14 \cdot 10^3$	0.998
PVA	2.69 ± 0.11	$2.29 \cdot 10^3$	0.996
PVP	3.06 ± 0.13	$2.05 \cdot 10^3$	0.996

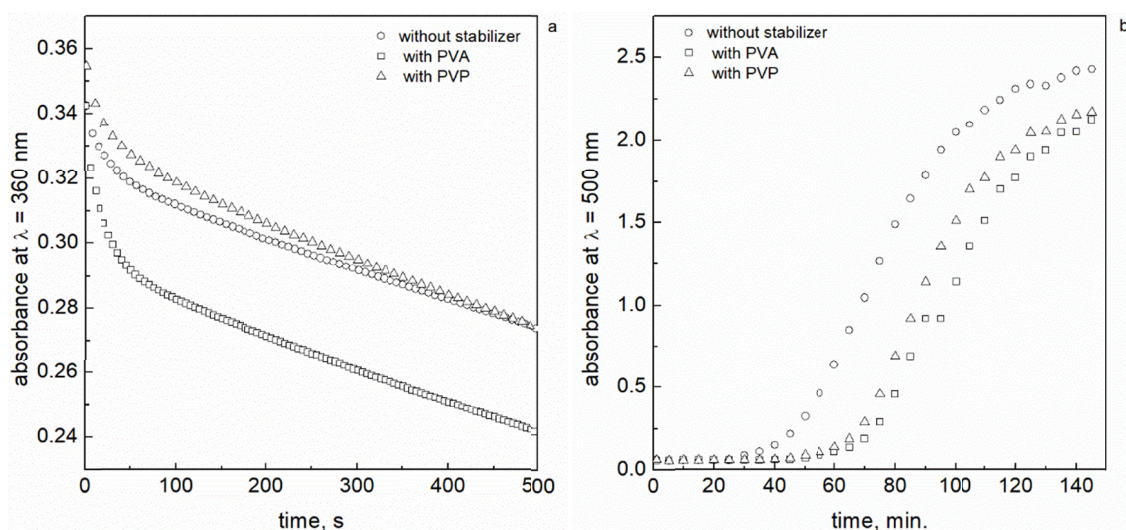


Fig. 5. Kinetic curve for reduction reaction of Pt(IV) ions with L-ascorbic acid (a) nucleation and growth (b) without and with PVA and PVP additions. Conditions: $C_{0,Pt(IV)} = 1.00 \text{ mM}$, $C_{0,H_2Asc} = 60 \text{ mM}$, $pH = 2.5 \pm 0.05$, $T = 313\text{K}$, $m_{polymer} : m_{Au(III)} = 10 : 1$

From obtained data (values of observed rate constants, Table 4) results that the nucleation and growth of gold nanoparticles is slower when polymers are added to the reacting solution.

3.3.2. Platinum nanoparticles formation

Similarly, kinetic experiments were performed for the reduction of Pt(IV) ions with ascorbic acid and sodium borohydride without and with polymer addition. As a results of reduction reaction of Pt(IV) ions with L-ascorbic acid, a decrease of absorbance at 360 nm was registered (Fig. 5a). This wavelength was selected, because at shorter wavelength i.e. 262 nm it is very close to the pick coming from ascorbic acid (at 246 nm) and spectra overlap. The process of reduction of platinum ions is quite slow in comparison to gold ion. The shape of obtained kinetic curves suggest that process of Pt(IV) reduction is more complex. Detailed kinetic study system without polymer [24] shows that the process reduction runs in two parallel paths. Thus, the differential equation describing the reduction reaction of Pt(IV) to Pt(II) ions takes the form:

$$-\frac{dC_{Pt(IV)}}{dt} = (k_{1a,obs} + k_{1b,obs}) \cdot C_{Pt(IV)} \quad (11)$$

where $k_{1a,obs}$ and $k_{1b,obs}$ – observed rate constants and $k_{1a,obs} = k_1 \cdot C_{H_2Asc}$, $k_{1b,obs} = k_2 \cdot C_{HAsc^-}$, k_{1a} and k_{1b} – first-order rate constants.

The change of Pt(IV) concentration in time can be described as:

$$C_{Pt(IV)} = C_{0,Pt(IV)} \exp(-k_{1a,obs}t) + \\ + C_{0,Pt(IV)} \exp(-k_{1b,obs}t) \quad (12)$$

where $C_{0,Pt(IV)}$, $C_{Pt(IV)}$ denote initial concentration of platinum ions and concentration at the “t” time, respectively.

Determined rate constants for the first step, i.e. reduction Pt(IV) to Pt(II) ions were gathered in Table 5.

TABLE 5

Observed rates constant for reduction reaction of Pt(IV) ions with L-ascorbic with and without stabilizer.
Conditions: $C_{0,Pt(IV)} = 1.0$ mM, $C_{0,H_2Asc} = 60$ mM, $T = 313$ K

Polymer	$(k_{1a,obs} \pm \sigma) \cdot 10^3, s^{-1}$	$k_1 \cdot 10 \pm \sigma, M^{-1}s^{-1}$	$(k_{1b,obs} \pm \sigma) \cdot 10^3, s^{-1}$	$k_2 \pm \sigma, M^{-1}s^{-1}$	R^2
without	42.10 ± 0.31	7.21 ± 0.05	0.32 ± 0.07	1.97 ± 0.43	0.999
PVA	49.92 ± 0.32	8.55 ± 0.05	0.39 ± 0.09	2.41 ± 0.55	0.999
PVP	41.65 ± 0.33	7.13 ± 0.06	0.37 ± 0.08	2.28 ± 0.49	0.999

The obtained results (observed rate constants, Table 5) show that the reduction process runs the fastest in the presence of PVA. The next stage during reduction process is Pt(II) transition to Pt(0), which results in platinum nucleus formation, which then autocatalytically grow. Such a mechanism is confirmed by the kinetic curves (Fig. 5b) registered at 500 nm, which have a sigmoid character. Therefore, to describe the mechanism of platinum particle formation as a result of reduction reactions of the Pt(IV) chloride complex with L-ascorbic acid, the Watzky-Finke model can be used. Given that the pseudo-primary rate of platinum(IV) ion reduction rate is two orders of magnitude greater than the k_{obs} value for the nucleation process (compare Table 5 and Table 6), the step limiting the formation of nuclei of the metallic phase is the reduction of Pt(II) ions to Pt(0). Therefore, it can be assumed that the initial concentration of Pt(II) ions in the system is equal to the initial concentration of Pt(IV) ions. Solving the differential equation (13) describing the kinetic curve of the nucleation and growth process and using mass balance (14) one can determine the linear form of the equation (15), on the basis of which the values of nucleation and growth rate constants were determined (Table 6).

$$\frac{dC_{Pt}}{dt} = (k_{n1,obs} + k_{n2,obs})C_{Pt(IV)} + (k_{g1,obs} + k_{g2,obs})C_{Pt(IV)}C_{Pt} \quad (13)$$

$$C_{0,Pt(II)} = C_{0,Pt(IV)} - C_{Pt(IV)} \quad (14)$$

where: $C_{0,Pt(II)}$ is the initial concentration of Pt(II) ions at the beginning of the formation process of colloidal particles.

$$\ln \frac{C_{Pt}}{C_{0,Pt(IV)} - C_{Pt}} = \ln \frac{(k_{n1,obs} + k_{n2,obs})}{(k_{g1,obs} + k_{g2,obs})C_{0,Pt(IV)}} + [(k_{n1,obs} + k_{n2,obs}) + (k_{g1,obs} + k_{g2,obs})C_{0,Pt(IV)}]t \quad (15)$$

Analogously, on the basis of our previous study [25] and the obtained results of kinetic reactions of reduction of Pt(IV)

ions to Pt(II) with sodium borohydride it is known that this step is fast and pseudo zero order. The integral form of kinetic equation, which describes the concentration change of platinum(IV) complex ions with time has the following form:

$$C_{Pt(IV)} = C_{0,Pt(IV)} - k_{1,obs}t \quad (16)$$

where $k_{1,obs} = k_1 C_{NaBH_4}$.

In order to find out how the rate of reduction of platinum ions with sodium borohydride is influenced by the addition of polymer, kinetic measurements were carried out analogously to the reduction with L-ascorbic acid and obtained kinetic curve were given in Fig. 6a.

From the obtained results (rate constant values, Table 7) and the appearance of kinetic curves (Fig. 6a) it follows that the reduction process runs the fastest when PVP was present in the system.

TABLE 7

Observed rates constant for reduction reaction of Pt(IV) ions with sodium borohydride with and without stabilizer.
Conditions: $C_{0,Pt(IV)} = 0.05$ mM, $C_{0,NaBH_4} = 3.0$ mM, $T = 298$ K

Polymer	$(k_{obs} \pm \sigma) \cdot 10^3, Ms^{-1}$	$k_1 \cdot 10^{-3} \pm \sigma, s^{-1}$	R^2
Without	0.059 ± 0.004	19.7 ± 1.33	0.992
PVA	0.039 ± 0.002	13.0 ± 0.67	0.995
PVP	0.401 ± 0.012	133 ± 4	0.996

The next stage is the transition of Pt(II) to Pt(0), which results in platinum nucleus formation, which then autocatalytically grow. Such a mechanism is confirmed by the kinetic curves (Fig. 6b), which have a sigmoidal character. Therefore, the Watzky-Finke model can be used to describe the mechanism of platinum particle formation as a result of reduction reactions of the Pt(IV) chloride complex with sodium borohydride. Knowing the equation describing the change in the concentration of Pt(IV)

TABLE 6

Observed rates constant for nucleation and growth of platinum nanoparticles as a result of Pt(IV) ions reduction with ascorbic acid with and without stabilizer. Conditions: $C_{0,Pt(IV)} = 1.0$ mM, $C_{0,H_2Asc} = 60$ mM, $T = 313$ K, $m_{polymer} : m_{Au(III)} = 10 : 1$

Polymer	$(k_{n1,obs} + k_{n2,obs}) \pm \sigma, s^{-1}$	$(k_{n1} + k_{n2}) \pm \sigma, M^{-1}s^{-1}$	$(k_{g1,obs} + k_{g2,obs}) \pm \sigma, M^{-1}s^{-1}$	R^2
Without	$(3.61 \pm 0.10) \cdot 10^{-4}$	$(6.02 \pm 0.16) \cdot 10^{-3}$	68.98 ± 2.13	0.999
PVA	$(2.07 \pm 0.09) \cdot 10^{-4}$	$(3.45 \pm 0.15) \cdot 10^{-3}$	37.12 ± 1.15	0.997
PVP	$(2.32 \pm 0.06) \cdot 10^{-4}$	$(3.86 \pm 0.10) \cdot 10^{-3}$	42.76 ± 1.35	0.998

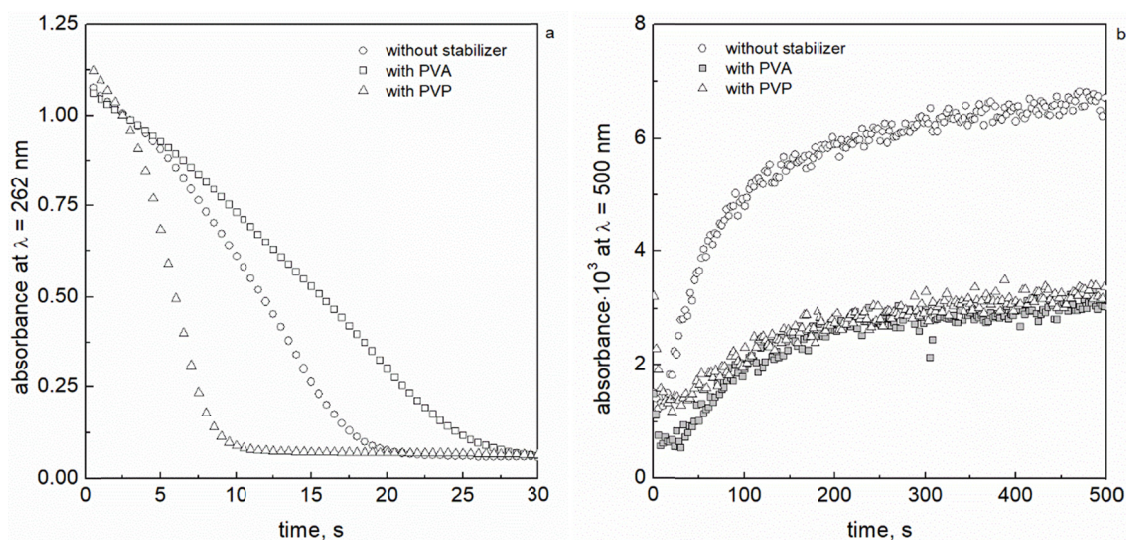


Fig. 6. Kinetic curve for reduction reaction of Pt(IV) ions with sodium borohydride (a) nucleation and growth (b) without and with PVA and PVP additions. Conditions: $C_{0,Pt(IV)} = 0.05$ mM, $C_{0,NaBH_4} = 3.0$ mM, $pH = 12.00 \pm 0.05$, $T = 298$ K, $m_{polymer} : m_{Au(III)} = 10 : 1$.

TABLE 8

Observed rate constants for nucleation and autocatalytic growth of platinum nanoparticles obtained as results reduction reaction between Pt(IV) with $NaBH_4$. Conditions: $C_{0,Pt(IV)} = 0.05$ mM, $C_{0,NaBH_4} = 3.0$ mM, $T = 313$ K, $I = 0.05$ M

Polymer	t_i , s	$(k_{2,obs} \pm \sigma) \cdot 10^3, s^{-1}$	$k_2 \pm \sigma, M^{-1}s^{-1}$	$k_{3,obs} \pm \sigma, M^{-1}s^{-1}$	R^2
Without	11	5.30 ± 0.07	1.77 ± 0.02	$(1.15 \pm 0.06) \cdot 10^3$	0.999
PVA	17	3.10 ± 0.12	1.03 ± 0.04	48.04 ± 0.12	0.997
PVP	15	4.83 ± 0.17	1.61 ± 0.06	$(1.97 \pm 0.12) \cdot 10^3$	0.996

ions in time and using the mass balance between Pt(IV) and Pt(II) ions, one can determine the equation on the basis of which the initial concentration Pt (II) ions was determined:

$$C_{0,Pt(II)} = C_{0,Pt(IV)}(1 - k_{obs}t_i) \quad (17)$$

where $C_{0,Pt(II)}$ denotes initial concentration of Pt(II) ions, t_i – incubation time.

Taking into account the fact that a large excess of the reducer was used in relation to platinum ions, one can write a differential equation describing the kinetic curve of the nucleation and growth process:

$$\frac{dC_{Pt}}{dt} = k_{g,obs}C_{Pt(II)} + k_{n,obs}C_{Pt(II)}C_{Pt} \quad (18)$$

after integration, the following relationship was obtained:

$$\ln \frac{C_{Pt}}{C_{0,Pt(II)} - C_{Pt}} = \ln \frac{k_{g,obs}}{k_{n,obs}C_{0,Pt(II)}} + (k_{g,obs} + k_{n,obs}C_{0,Pt(II)})t \quad (19)$$

From the linear form of the equation (19) the values of nucleation and growth processes were determined (Table 8).

In the examined system, registered kinetic curves (Fig. 6b) and the obtained values of nucleation and growth rate constants (Table 8) confirm that platinum nanoparticles appear the fastest in a polymer-free system.

3.4. DLS analysis

Samples of colloidal gold and platinum obtained during experiments were also analysed using DLS method, and the results are summarized in the Table 9.

TABLE 9

The values of radius (R_n) by number (n) of gold and platinum nanoparticles with standard deviation (σ). Initial concentration of Au(III) ions was fixed at 0.15 mM and for Pt(IV) at 1.00 mM (reaction with ascorbic acid) and 0.05 mM (with sodium borohydride)

Reductant	Polymer	Hydrodynamic radius ($R_N \pm \sigma$), nm
Au nanoparticles		
H ₂ Asc	without	polydisperse
	PVA	15 ± 5
	PVP	40 ± 14
NaBH ₄	without	1.5 ± 0.7
	PVA	2.2 ± 0.9
	PVP	9.0 ± 1.7
Pt nanoparticles		
H ₂ Asc	without	3.7 ± 1.5
	PVA	4.2 ± 1.3
	PVP	2.6 ± 0.8
NaBH ₄	without	2.4 ± 1.2
	PVA	4.5 ± 2.3
	PVP	3.2 ± 0.9

Gold nanoparticles obtained as a result of reduction of Au(III) ions with ascorbic acid show variable size. It was shown, that in an acidic medium, it was not possible to obtain stable particles without the addition of a stabilizing agent and particles were aggregated very quickly. The addition of polymer to the system allowed to stop the aggregation process for a long time (at least 1 month). When sodium borohydride was used as reductant of Au(III) ions, the size of obtained particles was similar. The size (hydrodynamic radius) of obtained platinum particles without and with polymer additions was also comparable (Table 9) regardless of the type of the reducer used.

4. Summary

Obtained results confirm that type of used stabilizer has a strong effect on the kinetic rate of overall process during nanoparticles formation. Moreover, one stabilizer may influence in different way depending on the metal ions. It was shown, that the polymer addition to the gold ions influence on kinetic rate of nucleation and autocatalytic growth both in case of ascorbic acid and sodium borohydride as reductant. The addition of PVA to gold ions reduced with L-ascorbic acid causes that the process of nucleation and autocatalytic growth slows down and the value of observed rate constants for nucleation changes from $3.79 \cdot 10^{-3}$ (without polymer) to $7.15 \cdot 10^{-5} \text{ s}^{-1}$ (with PVA) and for growth changes from $1.15 \cdot 10^3$ (without polymer) to $0.48 \cdot 10^2 \text{ s}^{-1} \text{ M}^{-1}$ (with PVA). However, the rate of the reduction reaction of Au(III) ions is practically unchanged. In case of using sodium borohydride the addition of polymer effects on the shape of kinetic curve for reduction of Au(III) and it suggests that mechanism of the process is changed. In case of Pt(IV) ions reduction with L-ascorbic acid, the process speeds up a little when PVA was added. Determined values of observed rate constants for nucleation and growth platinum nanoparticles decrease twice comparing to the system without polymer. When sodium borohydride was used as reductant, the influence of polymer addition on reduction reaction was observed. In the presence of PVP the reduction reaction proceeds faster and determined constant rates were 10 times higher in comparison to the solution without polymer. In consequence, the process of platinum nanoparticles nucleation also accelerates. PVA does not impact on kinetic rates, and determined observed values for reduction, nucleation and growth were similar to that obtained for solution without polymer. Obtained results i.e. rate constants may be useful in the process of nanomaterials synthesis, in particular in microflow.

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