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KINETICS AND MECHANISM OF THE REACTION OF GOLD(III) CHLORIDE COMPLEXES WITH FORMIC ACID

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Abstract

In this work, the results of kinetic studies of the redox reaction of gold(III) chloride complexes ($[AuCl_4]^-$) with formic acid, are presented. Obtained data suggest the complex character of the reaction which leads to the $[AuCl_2]^-$ and $[AuCl_3(COOH)]^-$ ions formation as intermediates. In the pH range over 2.5, the final product of the reaction is metallic gold. From the analysis of kinetic data, the rate limiting step is found to be the gold metallic phase formation. The stage of Au(III) reduction is relatively fast with the second-order rate constant equal to 61.8 $M^{-1}s^{-1}$ at temperature 50 ^oC. The rate of the studied reaction depends on the temperature, reactants concentration and chloride ions concentration. As a result of the data analysis, the scheme of the reaction path has been suggested. Also, the values of enthalpy and entropy of activation for the reaction have been determined.

Keywords: Kinetics, Mechanism of Reaction, Redox Reaction, Gold(III) complex, Formic Acid

1. Introduction

In the recent years, the production of gold and platinum group metals has become important due to the growth in demand for these metals, as well as their limited resources, political situation, competition on the market, etc. Thus, the producers are not able to provide adequate supply.

The variety of methods used for the recovery and production of precious metals depends on the type of sources (primary or secondary raw materials) containing a metal. In modern methods of recovery, hydrometallurgical approach is very often used. However, this method sets specific requirements related to the effectiveness and efficiency of the method, to the minimum hazard in contact with the environment, etc.

Hydrometallurgical methods of gold recovery are based on the transfer of precious metals into solution by the leaching liquids (e.g. „chlorine water" [1], ammonia [2], thiocyanates [3], thiourea [4]), followed by their recovery from the solution, preferably selectively. For this purpose, the most commonly used processes are: electrolysis [5], chemical sorption in the ion exchange columns [6], adsorption on the carbon materials [7], precipitation of the metallic phase by reduction [8]. In the industry, the precipitation of metallic phase of the elements as an effect of induced redox reaction is very often used. However, the metallic solid phase precipitation from the solutions can encounter a number of difficulties. In example, as a result of inappropriate choice of the reductant, as well as the reaction conditions for the given system, the solid phase formation is not possible. Among others, the non-selective precipitation of the main metal from a solution containing other metals can take place.

There are numerous reducing agents used for the gold solid phase precipitation from aqueous solutions, e.g.: formaldehyde [9], sodium borohydride [10] hydrazine [11], sodium citrate [12], tartrates [13], glucose [14], dimethylamine borane [15], free radicals [16], sodium formate [17]. The last one is even used in the KGHM Polska Miedź S.A. copper plant as a reductant of Pt(IV) and Pd(II) ions at the stage of "sludge Pt-Pd" precipitation from an aqueous solution containing chloride ions of gold(III).

There are only a few literature sources on the kinetics and mechanism of the reaction of gold(III) chloride ions with formate. From these data it is known that at room temperature, carboxylic acids react very slowly with the gold(III) chloride complexes in aqueous solutions [18]. According to Maritz and Van Eldik [19] the rate constant of the $[AuCl_4]^-$ reaction with formic acid in aqueous HCl solution (pH = 3.5, temp. 50 °C) is equal to $k_{obs} = 3.0 - 9.0 \cdot 10^{-5}\ s^{-1}$). It is also known that the metallic particles of platinum or palladium present in the

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system catalyze the oxidation reaction of HCOOH [20]. Thus, they contribute to the inhibition (by increasing formic acid concentration) of the reduction reaction of Au(III) to Au(0).

From the analysis of literature data [21, 22] it can be suggested that the change of acidity of the solution can affect the kinetics and mechanism of the gold(III) reaction reduction, leading under proper conditions to gold precipitation from the solution. In this paper we described the results of the kinetic studies of the reduction reaction of chloride gold(III) complex ions with formic acid in weak acidic solutions (pH = 2.9). We believe that the knowledge of the kinetics of gold(III) reduction reaction using formic acid can be a helpful in selection of the optimal conditions for selectivity of the reduction reaction of Au(III) ions in the presence of Pt(IV) and Pd(II) ions in the solution.

2. Experiments

2.1 Chemicals

In our experiments the following chemicals and substances were used:

- 0.1 M tetrachloroauric acid ($HAuCl_4$) (Mennica Panstwowa, Warszawa, Poland) - used as a base solution. Prepared by dilution of pure gold (99,99%) in *aqua regia* and purified with HCl to remove the nitrate.
- 98÷100% formic acid (HCOOH) (MERCK KGaA, Germany) - used as a reductant of gold(III) ions.
- 35÷38% hydrochloric acid (HCl) (CHEMPUR, Piekary Slaskie, Poland) and sodium hydroxide (NaOH) (Zaklady Chemiczne Oswiecim, Poland) – used to keep the pH constant.
- Sodium chloride (NaCl) (PPH „POCh" SA Gliwice, Poland) – used to keep the proper concentration of Cl^- in the system.
- Sodium perchlorate ($NaClO_4$) (Koch–Light Laboratories Ltd., UK) – used to adjust the ionic strength in electrolyte.
- Deionizing water – used as a solvent.

The gold(III) solutions were freshly prepared prior the experiments by the dilution of proper amount of the 0.1 M $HAuCl_4$ in 0.1 M HCl and 0.1 M NaOH to rich the pH = 2.9. Analogically, the aqueous solutions of formic acid with the proper concentration have been prepared.

2.2. Apparatus and methodology

The kinetic measurements were performed using classical UV-Vis spectrophotometry (Shimadzu, U-2501 PC, Kyoto, Japan) and stopped-flow technique (Applied Photophysics model SX-20) under isothermal conditions. Based on the change in absorption of reactants in the range of wavelength from 190 to 900 nm, the kinetic curves (absorbance vs. time) have been determined.

To analyze the colloidal gold particles precipitated in the solution, turbidimetric and photon correlation spectroscopy methods were used for measuring the changes of beam intensity of visible light and dynamic light scattering (Zetasizer Nano, Malvern Instruments, UK) after passing through the tested circuit, respectively.

Spectrophotometric measurements consisted in injecting of reactant solutions in a volume ratio of 1:1 to a spectrophotometer quartz cuvette. The stopped-flow technique used a pneumatically driven system for rapid mixing (ms range) of the reactants, coupled with the diode array detection system. This made it possible to register changes in absorbance during the reaction and to obtain the kinetic curves. All registered data were collected at a wavelength 314 nm, characteristic of $[AuCl_4]^-$ complexes and 580 nm, characteristic of colloidal gold, as well. To describe the experimental data the fitting of appropriate form of the rate equation using Pro-Data Viewer and OriginPro 8 software have been applied. Further, using these data, the values of the rate constant have been determined.

All experiments were carried out under conditions summarized in Table 1.

3. Results

3.1 The composition of reactants solutions – calculation

Depending on pH of aqueous solution, the gold(III) complexes [23] and the formic acid [24] can exist in different forms. Calculated equilibrium compositions of these solutions are shown in Fig. 1a and Fig. 1b.

The diagrams analysis provides information which reactant form may be involved in the reaction, under the conditions of experiments.

3.2 The Spectra of Solutions

The presence of complex form of gold(III) in the studied system, as a form of a chloride complex, was spectrophotometrically confirmed (Fig. 2). The absorption band with a maximum at a wavelength 314 nm corresponds to $[AuCl_4]^-$. HCOOH does not absorb the light in the range from 250 to 900 nm in the aqueous solution.

After mixing of the reactants, disappearance of the absorption band at $\lambda = 314$ nm was observed (Fig. 3). This indicates that the reduction reaction of gold(III) ions in the solution takes place. Simultaneously, the new band in the visible part of the spectrum, with $\lambda_{max} = 580$ nm, appears in the system. It is characteristic of the plasmon absorption band derived from the

Table 1. *Conditions under which experiments of the reaction kinetics of* $[AuCl_4]^-$ *with formic acid have been carried out.*

Concentration of $[AuCl_4]^-$ [mM]	Concentration of HCOOH [mM]	Temperature	Concentration of Cl^- [M]	Ionic Strength [M]	pH
Effect of HCOOH concentration on the rate constant					
0.15	1.5	50	0.1	0.05	2.9
	3				
	4.5				
	6				
	7.5				
Effect of $[AuCl_4]^-$ initial concentration on the rate constant					
0.05	5	50	0.1	0.05	2.9
0.1	10				
0.15	15				
0.2	20				
Effect of ionic strength on the rate constant					
0.15	1.5	50	0.1	0.55	2.9
				0.11	
				0.165	
				0.22	
				0.25	
Effect of temperature on the rate constant					
0.15	1.5	35	0.1	0.05	2.9
		40			
		45			
		50			
Effect of Cl^- concentration on the rate constant					
0.15	1.5	50	10	0.05	2.9
			20		
			30		
			40		
			50		

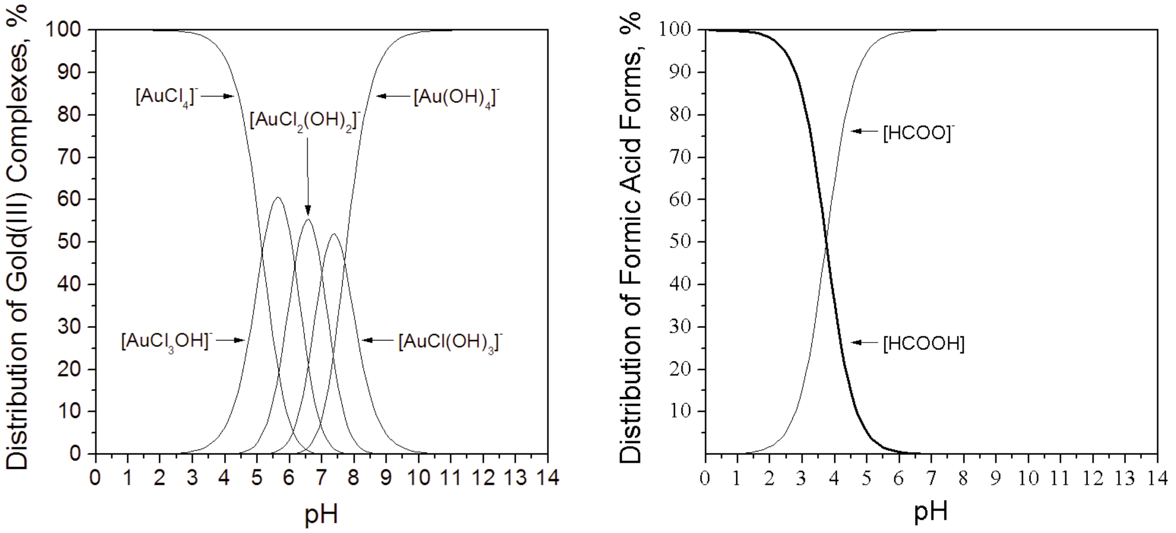

Figure 1. *Distribution of the gold(III) chloride complexes (a) and the equilibrium forms of formic acid (b) as a function of pH at temperature 50* °*C and concentration of chloride ions* $C_{Cl^-} = 0.1$ *M. In calculations, the equilibrium constants of* $[AuCl_4]^-$ *hydrolysis from [8] and dissociation constant of formic acid from [24], were used.*

collective resonance of electrons at the surface of colloidal gold. This fact indicates that the reduction of gold(III) by formic acid leads to the gold solid phase formation.

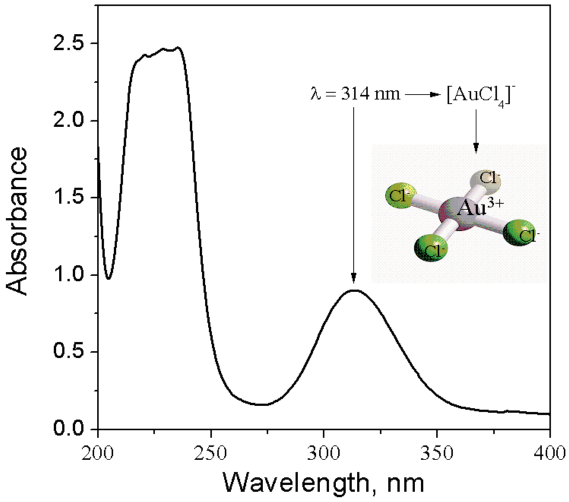

Figure 2. *Absorption spectrum of the* $[AuCl_4]^-$ *with the maximum at λ = 314 nm in the range of wavelength 200-400 nm. Experimental conditions:* $C_{0,Au(III)} = 0.15$ *mM, pH = 2.9, temperature (50±0.1)* ^oC.

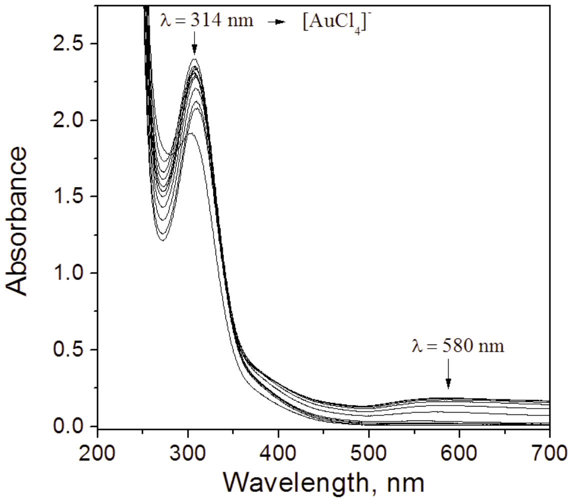

Figure 3. *The decrease of intensity of* $[AuCl_4]^-$ *absorption band (λ = 314 nm) and increase of plasmon absorption band (λ = 580 nm) during the reaction with HCOOH. Experimental conditions:* $C_{0,Au(III)} = 0.15$ *mM;* $C_{0,HCOOH} = 15$ *mM; pH = 2.9; temperature (50±0.1)* ^oC.

Following registered spectra, it was assumed that the first step of the redox reaction is described as:

$$[AuCl_4]^- + HCOOH \xrightarrow{k_1} products \tag{1}$$

For the reaction (1), the rate equation has a form:

$$-\frac{dC_{[AuCl_4]^-}}{dt} = k_1 \cdot C^{\alpha}_{[AuCl_4]^-} \cdot C^{\beta}_{HCOOH} \tag{2}$$

When the reaction with a large excess of reductant is carried out, formic acid concentration can be assumed constant during the reaction. In such a case, the equation (2) has a form:

$$-\frac{dC_{[AuCl_4]^-}}{dt} = k_{obs} \cdot C^{\alpha}_{[AuCl_4]^-} \tag{3}$$

where:

$$k_{obs} = k_1 \cdot C^{\beta}_{HCOOH} \tag{4}$$

The proportionality of $k_{obs} \sim C_{HCOOH}$ in eq. (4) and thus the validity of assumption (3) can be verified by the experiment. The results of this experiment are shown in the next section.

3.3 Effect of Reductant Concentration

The form of the kinetic equation fitted to experimental curves:

$$C_{Au(III)} = C_{0,Au(III)} exp\left(-k_{obs} \cdot t\right) \tag{5}$$

indicates that under isolation conditions (large excess of reductant concentration) the pseudo-first-order reaction of gold(III) complexes takes place. Experimentally determined effect of the HCOOH concentration on the observed rate constant (k_{obs}) is shown in Table 2 and in Fig. 4.

Table 2. *Influence of the reductant concentration on the observed rate constant* (k_{obs}) *for the reaction of* $[AuCl_4]^-$ *with HCOOH in the solution with pH = 2.9. Conditions:* $C_{0,Au(III)} = 0.15$ *mM; temperature (50±0.1)* ^oC.

Initial Concentration of HCOOH [mM]	The Rate Constant k_{obs} [s^{-1}]	Average of k_{obs} [s^{-1}]	Mean Standard Deviation [s^{-1}]
1.5	0.367	0.377	± 0.010
	0.379		
	0.386		
3	0.434	0.416	± 0.055
	0.354		
	0.459		
4.5	0.643	0.592	± 0.055
	0.599		
	0.534		
7.5	0.726	0.727	± 0.13
	0.598		
	0.856		

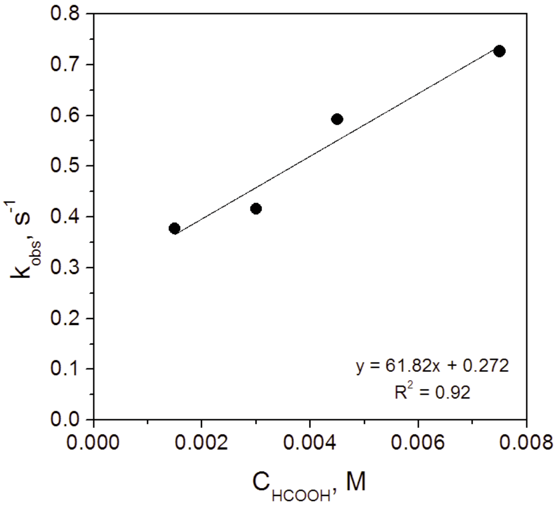

Figure 4. *Dependence of k_{obs} vs. C_{HCOOH} for the reaction of $[AuCl_4]^-$ with formic acid at pH = 2.9. The other experimental conditions: $C_{0,Au(III)}$ = 0.15 mM; temperature (50±0.1) °C; I = 0.05 M.*

The linear increase of k_{obs} with the increase of reductant concentration and the presence of intersection at the k_{obs} axis (Fig. 4) for $C_{HCOOH} = 0$ indicates the necessity of the verification of equation (4) and its complementation with the constants 0.272 s^{-1}. This interception suggests the existence of a parallel path of the $[AuCl_4]^-$ reaction, resulting probably from the presence of the second form of reductant in the system ($COOH^-$) (Fig. 1b). This reaction can be written as:

$$[AuCl_4]^- + COOH^- \xrightarrow{k_2} products \tag{6}$$

3.4 Effect of Gold(III) Initial Concentration

To determine the reaction order with respect to $[AuCl_4]^-$ complex ions, initial rate method was used. By this method, the reaction rate was measured at the beginning of its course using different initial concentrations of $[AuCl_4]^-$ and constant excess (100-fold) of the reductant with respect to the gold(III) concentration. The resulting rate constants are shown in Table 3.

Assuming that the rate of every parallel step of gold(III) reduction has a form:

$$V_o = k_{obs} \cdot C^{\alpha}_{[AuCl_4]^-} \tag{7}$$

where V_0 is the rate of the reaction at the very beginning and α is the reaction order with respect to $[AuCl_4]^-$, after taking the logarithm of (7), we can obtain the linear form of this equation:

$$\log V_o = \log k_{obs} \cdot \alpha \cdot \log C_{[AuCl_4]^-} \tag{8}$$

Table 3. *The observed rate constant for the reaction of $[AuCl_4]^-$ with HCOOH at different initial concentration of $[AuCl_4]^-$ in solution with pH = 2.9. The other experimental conditions: 100-fold excess of reductant concentration; I = 0.05 M $NaClO_4$; temperature (50±0.1) °C.*

Initial Concentration of Gold(III) [mM]	The Rate Constant k_{obs} [s^{-1}]	Average of k_{obs} [s^{-1}]	Mean Standard Deviation [s^{-1}]
0.05	0.281	0.275	± 0.010
	0.279		
	0.263		
0.1	0.275	0.276	± 0.003
	0.279		
	0.273		
0.15	0.305	0.312	± 0.006
	0.315		
	0.315		
0.2	0.336	0.346	± 0.009
	0.348		
	0.353		

The obtained results of k_{obs} described in accordance with eq. (8) have a linear character (Fig. 5). It can be noticed that the value of α is equal to 1.16 which at isolation conditions (large excess of the reductant) indicates the pseudo-first-order character of the gold(III) reduction reaction.

Also, after recalculation of the k_{obs} from Table 2 and taking the logarithm from equation (4):

$$ln(k_{obs}) = ln(k_1) + \beta\, ln(C_{HCOOH}) \tag{9}$$

the order of reaction with respect to formic acid ($\beta \approx 0.5$) have been determined (Fig. 6).

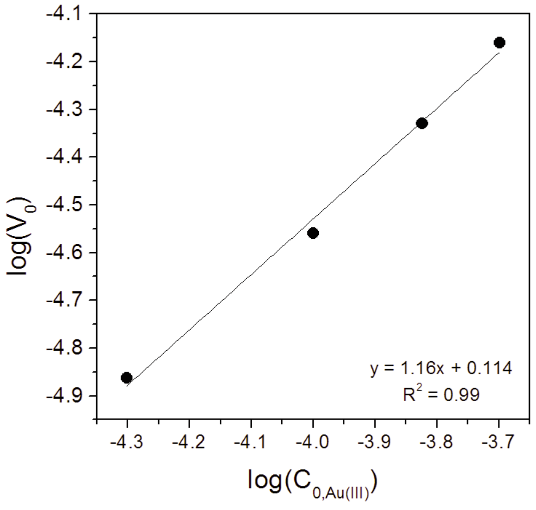

Figure 5. *Dependence of log (V_0) vs. log ($C_{0,Au(III)}$) for the parallel reactions of $[AuCl_4]^-$ with the formic acid - the value of the slope indicates the order of reaction with respect to $[AuCl_4]^-$.*

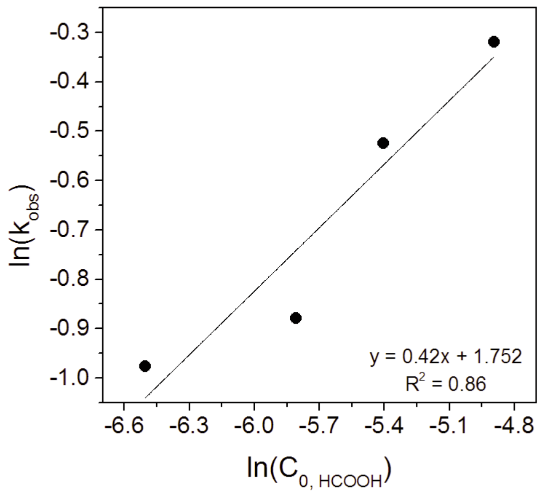

Figure 6. *Dependence of ln(k_{obs}) vs. ln($C_{0,HCOOH}$) - the value of the slope indicates the order of reaction with respect to HCOOH.*

3.5 Effect of Ionic Strength

In order to determine the kind of charges of reacting species in the system, the salt effect has been studied. Obtained kinetic results showed that at pH = 2.9 (Table 4) the rate constant (k_{obs}) of the reaction is not dependent on the ionic strength. From this fact, as well as from the analysis of Brönsted-Bjerrum (BB) relationship (($k_{obs}/k_{0,obs}$) vs. $\sqrt{I}/(1 + \sqrt{I})$ [25]), the neutral character of the reductant can be suggested (Fig. 7).

Table 4. *The values of the rate constant (k_{obs}) for the reaction of $[AuCl_4]^-$ with HCOOH at different ionic strength. Experimental conditions: pH = 2.9; temperature (50±0.1) °C; $C_{0,Au(III)}$ = 0.15 mM; $C_{0,HCOOH}$= 1.5 mM.*

Ionic Strength [mM]	The Rate Constant k_{obs} [s^{-1}]	Average of k_{obs} [s^{-1}]	Mean Standard Deviation [s^{-1}]
55	0.296	0.288	± 0.007
	0.283		
	0.285		
110	0.261	0.264	± 0.024
	0.241		
	0.289		
165	0.291	0.296	± 0.006
	0.303		
	0.295		
220	0.266	0.265	± 0.006
	0.258		
	0.27		
250	0.252	0.271	± 0.017
	0.274		
	0.285		

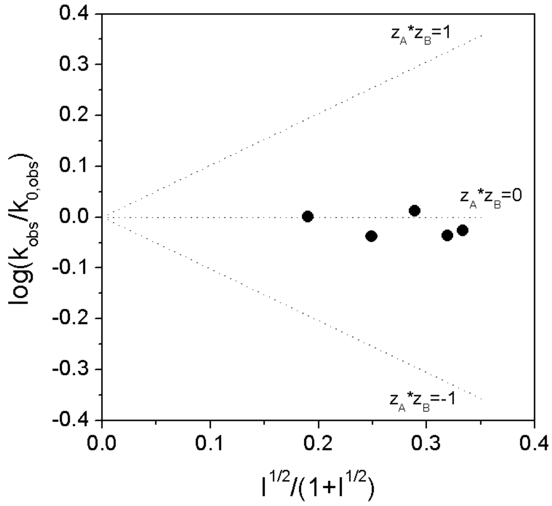

Figure 7. *Brönsted–Bjerrum dependence [25] for the reaction of $[AuCl_4]^-$ with HCOOH. Experimental conditions: pH = 2.9, temperature (50±0.1) °C; $C_{0,Au(III)}$= 0.15 mM; $C_{0,HCOOH}$= 1.5 mM.*

3.6 Effect of Temperature

In order to determine the enthalpy (ΔH^*) and entropy (ΔS^*) of activation of the reaction, kinetic measurements were carried out at different temperatures: 35, 40, 45 and 50 °C, respectively. The values of the obtained rate constants are summarized in Table 5.

Table 5. *The values of the rate constant (k_{obs}) for the reaction of $[AuCl_4]^-$ with HCOOH at different temperatures. Experimental conditions: $C_{0,Au(III)}$ = 0.15 mM; $C_{0,CHOOH}$= 1.5 mM; pH = 2.9; I = 0.05 M.*

Temperature	The Rate Constant k_{obs} [s^{-1}]	Average of k_{obs} [s^{-1}]	Mean Standard Deviation [s^{-1}]
308	0.0667	0.0681	± 0.0016
	0.0676		
	0.0699		
313	0.0932	0.0942	± 0.0010
	0.094		
	0.0954		
318	0.113	0.113	± 0.001
	0.113		
	0.111		
323	0.135	0.138	± 0.003
	0.14		
	0.139		

Using linear form of the Eyring dependence:

$$ln\left(\frac{k}{T}\right) = 23.759 + \frac{\Delta S^*}{R} - \frac{\Delta H}{R}\cdot\frac{1}{T} \tag{10}$$

as well as graphical method (Fig. 8), values of ΔH^* and ΔS^* were found to be 35.44 [kJ·mol^{-1}] and -152 [J·mol^{-1}·K^{-1}], respectively.

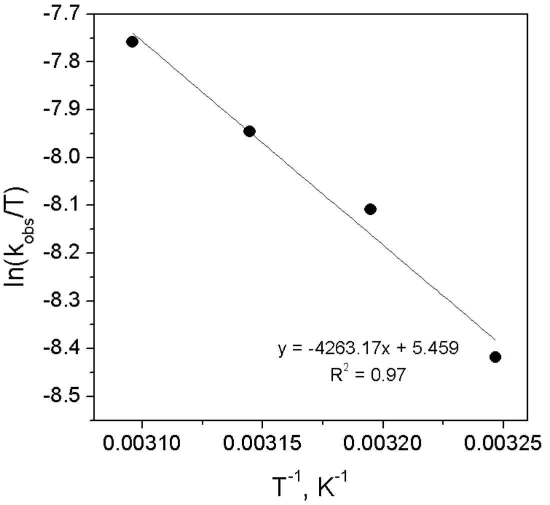

Figure 8. *The Eyring dependence for the reaction of* $[AuCl_4]^-$ *with HCOOH. Experimental conditions:* $C_{0,Au(III)} = 0.15$ *mM;* $C_{0,HCOOH} = 1.5$ *mM; pH = 2.9; I = 0.05 M.*

3.7 Effect of Chloride Ions Concentration

In order to determine the influence of Cl^- on the rate constant of the reaction, the measurements were carried out in solutions with various NaCl concentrations. Obtained values of the k_{obs} are shown in Table 6.

Table 6. *The values of the rate constant for the reaction of* $[AuCl_4]^-$ *with HCOOH at different* Cl^- *concentration. Experimental conditions:* $C_{0,Au(III)} = 0.15$ *mM;* $C_{0,HCOOH} = 0.75$ *mM; pH = 2.9; I = 0.05 M, temperature (50±0.1) °C.*

Concentration of Cl^- [M]	The Rate Constant k_{obs} [s^{-1}]	Average of k_{obs} [s^{-1}]	Mean Standard Deviation [s^{-1}]
0.01	0.773	0.724	± 0.079
	0.619		
	0.778		
0.02	0.694	0.666	± 0.302
	0.683		
	0.621		
0.03	0.674	0.68	± 0.131
	0.591		
	0.776		
0.04	0.786	0.746	± 0.068
	0.713		
	0.739		
0.05	0.667	0.648	± 0.256
	0.64		
	0.637		

Small changes in the value of k_{obs} may provide a negligible impact of Cl^- concentration on the reaction rate constant under these conditions. The empirical relationship of k_{obs} as a function of Cl^- may be described by the equation:

$$k_{obs} = -0.719 \cdot C_{Cl-} + 0.714 \qquad (11)$$

which is valid in the range of Cl^- concentration from 0.01 to 0.05 M (Table 6).

3.8 Effect of pH

The organoleptic analysis of the samples containing gold(III) ions, 48 hours after injection of reductant at different acidity indicates that in the range of pH from 2.5 to 4.0 the solid phase of gold is formed (Fig. 9). However, the morphology of these precipitates depends on the acidity. In the solution with pH = 2.5 and 2.9 the brown precipitate at the bottom of the sample was present. In the solution with pH = 4.0, the colloidal phase of gold is formed.

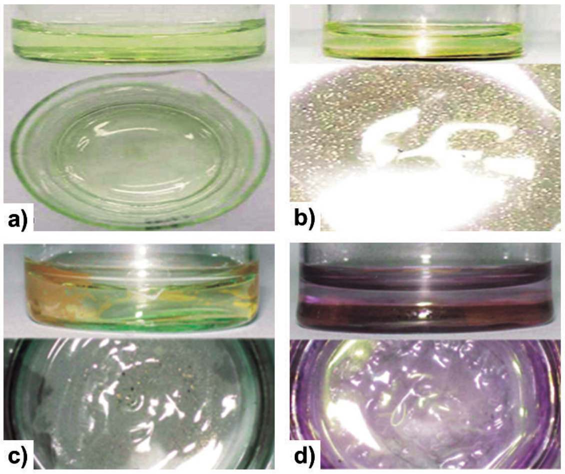

Figure 9. *The pictures of solutions after 48 hours from the mixing of 0.15 mM* $HAuCl_4$ *with 150 mM HCOOH at different pH conditions: a) pH = 1 – the lack of gold precipitate; b) pH = 2.5 – gold precipitate; c) pH = 2.9 – gold precipitate; d) pH = 4.0 – gold as a colloid; temperature 50 °C.*

From the analysis of the spectrum of reacting solution in the UV-Vis range, the presence of plasmon absorption band was registered with the maximum at $\lambda = 580$ nm. That is the evidence of the colloidal gold formation in the solution. It enables us to measure the progress of colloidal gold formation using turbidimetric as well as DLS methods. The examples of registered kinetic curves are shown in Fig. 10 and Fig. 11, respectively. The turbidimetric curves indicate that the time (τ) necessary for metallic gold particles precipitation (characteristic of maximum value of absorbance) is shortened when pH increases, e.g. the change of pH from 2.9 to 4.0 results in the change of τ from ca. 27000 to 15000 s.

Clear evidence for the coagulation and growth of the gold particles during the reaction can be derived from DLS studies. As an example, the continuous growth of the hydrodynamic radius of the particles was registered in solution with pH = 2.9 (Fig. 11). As a result, the particles reached ca. 60 nm in diameter and after that they coagulated to the larger conglomerates. Finally, they precipitate in the reactor as a powder with diameter of µm, in order of magnitude. Opposite behavior of gold particles was observed at pH = 4.0. Under these conditions they were stable as a colloid for days.

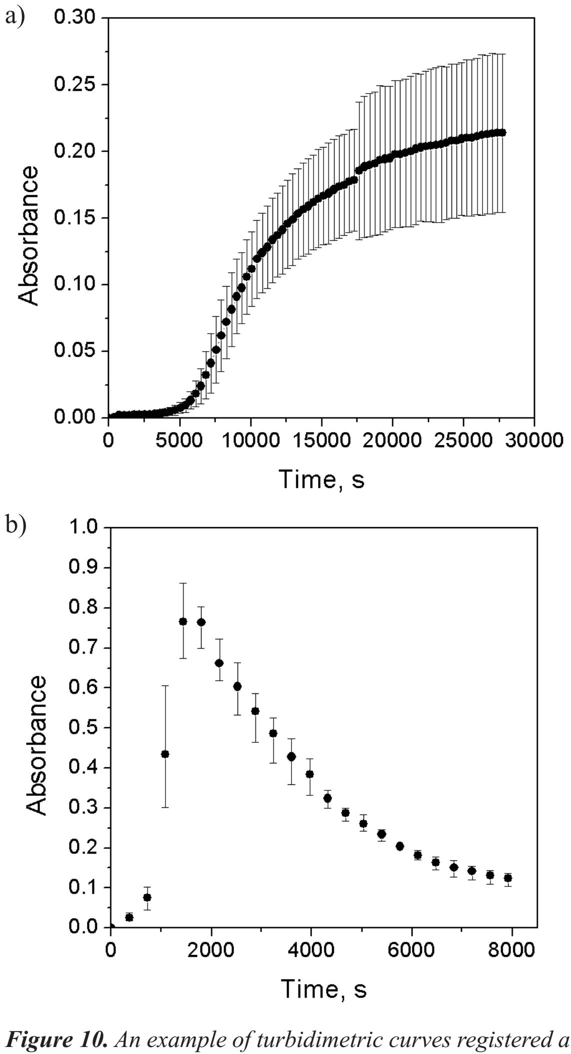

Figure 10. *An example of turbidimetric curves registered at λ = 580 nm during the gold particles formation in the reaction of $[AuCl_4]^-$ with CHOOH: a) pH = 2.9; b) pH = 4.0. Experimental conditions: $C_{0,Au(III)}$ = 1.5 mM, $C_{0,CHOOH}$ = 150 mM, temperature (50±0.1) °C.*

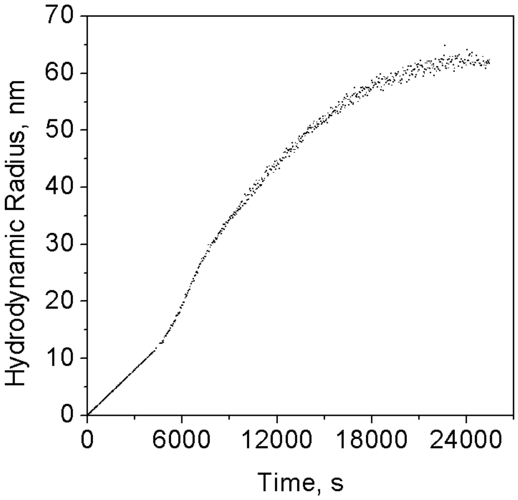

Figure 11. *An example of kinetic curve, hydrodynamic radius vs. time, registered using DLS method for the gold particles formation in the reaction of $[AuCl_4]^-$ with HCOOH. Experimental conditions: $C_{0,Au(III)}$ = 1.5 mM, $C_{0,CHOOH}$ = 150 mM, temperature (50±0.1) °C.*

4. Discussion and Conclusions

From the analysis of the equilibrium diagrams of the reactants (Fig. 1a and Fig. 1b) in a weak acidic environment (pH = 2.9), the ionic form of the gold(III) complexes, i.e. $[AuCl_4]^-$, and two forms of the reductant, i.e. HCOOH and $COOH^-$, are dominated species. Potentially, they can take part in a first step of the redox reaction. Experimental confirmation of the presence of $[AuCl_4]^-$ in solution and the participation of this complex in the reaction is the presence of absorption bands in the spectrum of the solution with a maximum at a wavelength λ = 314 nm and the decrease in absorbance at this wavelength after the addition of formic acid (Fig. 3).

Mathematical analysis of the recorded kinetic curves indicates the presence of the first-order reaction as the first step of the gold(III) reduction. Under the isolation conditions, applied during the experiments (large excess of reductant with respect to the gold(III) ion concentration), it suggests bimolecular character of this reaction:

$$[AuCl_4]^- + HCOOH \rightarrow [AuCl_2]^- + CO_2 + 2H^+ + 2Cl^- \qquad (12)$$

From further studies, including the effect of reductant concentration on the reaction rate, it is clearly seen that the observed rate constant k_{obs} increases linearly with HCOOH concentration (Fig. 4). Obtained empirical equation describing this relationship has the form:

$$k_{obs} = 30.75 \cdot C_{HCOOH} + 0.274 \qquad (13)$$

and shows the presence of intersection point with the k_{obs} axis in the $k_{obs} = f(C_{HCOOH})$ function. It suggests the parallel step in the redox reaction at this pH. It is very likely that the second (ionized) form of the reductant present at this pH reacts with the gold(III) complexes:

$$[AuCl_4]^- + COOH^- \rightarrow [AuCl_2]^- + CO_2 + H^+ + 2Cl^- \quad (14)$$

As a result of substitution of eq. (13) into eq. (4), the integral form of the kinetic equation describing disappearance of $[AuCl_4]^-$ in the system can be given:

$$C_{[AuCl_4]^-} = e^{-(30.75 \cdot C_{CHOOH} + 0.274)} \times C_{0,[AuCl_4]^-} \quad (15)$$

The order of the reaction with respect to $[AuCl_4]^-$ (α ≈ 1) (Fig. 5), as well as the order of reaction with respect to HCOOH (β ≈ 0.5), confirms the complexity of the reduction of gold(III) ions.

The lack of the effect of ionic strength on the reaction rate constant and the location of the experimental points along the theoretical curve, characteristic of neutral form of reagent (Fig. 7), leads to the conclusion that, in accordance to Bronsted-Bjerrum theory, the reductant has a molecular form. This form can react with ionic form of gold(III) chloride complex under conditions experiments were carried out.

The analysis of temperature effect on the rate constant of the reaction indicates that k_{obs} increases with the temperature and the Eyring equation is fulfilled. The enthalpy and entropy of activation possess the values typical for homogeneous reactions in aqueous solution.

The influence of chloride ions on the reaction rate constant is described by the empirical relationship (11). In the range of Cl^- concentrations from 0.01 to 0.05 M, the slope is equal to -0.5 and indicates a relatively slight decrease of k_{obs} value with the increase of Cl^- concentration. The resulting experimental data are consistent with those obtained for example by Maritz and Van Eldik [18], indicating the inhibitory role of the chloride ions in the redox reaction of the $[AuCl_4]^-$ complexes.

The mechanism of the metallic gold formation leads through the intermediate step of gold(I) formation in the form of $[AuCl_2]^-$. Analogically to the gold(III) ions, $[AuCl_2]^-$ is further reduced by the both forms of formic acid giving the Au as a product of the reaction:

$$\left[AuCl_2\right]^- + HCOOH \xrightarrow{k_3} Au + CO_2 + 2H^+ + 2Cl^- \quad (16)$$

$$\left[AuCl_2\right]^- + COOH^- \xrightarrow{k_4} Au + CO_2 + H^+ + 2Cl^- \quad (17)$$

These reactions are relatively slow under studied conditions. It cannot be excluded that the metallic phase of gold appears also as a result of $[AuCl_2]^-$ disproportionation as was described e.g. in [8]. Maritz and Van Eldik [19] suggested the mechanism which is based on the assumption that prior to electron transfer in the reduction reaction of gold(III) complex ions the short-lived intermediate compound is formed:

$$\left[AuCl_4\right]^- + HCOOH \xleftrightarrow{v.fast} \left[AuCl_4 \times HCOOH\right]^- \quad (18)$$

Because the halogen ligands in gold complexes can be substituted by other organic ligands (e.g. acetate [26]), after substitution of Cl^- ligand by the formate in coordination sphere the mixed gold(III)-formate complex is created:

$$\left[AuCl_4 \times HCOOH\right]^- \xrightarrow{k_1} \left[AuCl_3 \cdot COOH\right]^- + H^+ + Cl^- \quad (19)$$

Summarizing, the solid phase of gold can be formed in the reaction of gold(III) chloride complexes with formic acid in aqueous solutions. The best pH condition for the reaction is the range of pH from 2.5 to 2.9. In more acidic solution (pH = 1.0) and in solutions with pH over 4.0 either lack of gold solid phase is observed or colloidal gold is formed, respectively.

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