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KINETICS AND MECHANISM OF THE REDOX REACTION BETWEEN Pt(IV) CHLORIDE COMPLEX IONS AND SODIUM THIOSULFATE IN AQUEOUS SOLUTION. PART I: ACIDIC SOLUTION

KINETYKA I MECHANIZM REAKCJI REDOX POMIĘDZY CHLORKOWYMI JONAMI KOMPLEKSOWYMI Pt(IV) I TIOSIARCZANEM SODU W ROZTWORACH WODNYCH. CZĘŚĆ I: ROZTWÓR KWAŚNY

In this work, spectrophotometric studies of the kinetics and mechanism of reaction between $[PtCl_6]^{2-}$ complex ions and sodium thiosulfate, were carried out. The influence of different conditions, such as: initial concentrations of reductant and platinum(IV) complex ions, ionic strength, pH and temperature on the rate constant, was experimentally determined. From the obtained results, the molecularity of the first elementary step, value of the enthalpy and entropy of activation in Eyring equation as well as corresponding rate equation, were experimentally determined. It was found that the reaction is relatively slow and leads to the S, Pt and PtS colloids formation. The best conditions for solid phase formation containing Pt are at pH = 5.

Keywords: platinum complexes, thiosulfate, redox reaction, kinetics, rate law, rate constant

W pracy przedstawiono wyniki badań spektrofotometrycznych kinetyki i mechanizmu reakcji jonów kompleksowych $[PtCl_6]^{2-}$ z tiosiarczanem sodu. Doświadczalnie określono wpływ różnych czynników na stałą szybkości reakcji, tj.: stężenia początkowego reagentów, siły jonowej, pH oraz temperatury. Na podstawie otrzymanych wyników wyznaczono cząsteczkowość pierwszego etapu elementarnego reakcji, wartości entalpii i entropii aktywacji reakcji oraz równanie kinetyczne. Wykazano, że reakcja jest stosunkowo wolna i prowadzi do powstania koloidu złożonego z siarki, platyny oraz siarczku platyny (PtS). Najlepsze warunki do wytrącania koloidu zawierającego Pt to pH = 5.

1. Introduction

One of the possible methods used for the separation of noble metals is their precipitation from aqueous solutions [1]. This kind of reaction is frequently used in hydrometallurgical technologies [2]. For example, Au(III) complex chloride ions can be reduced by $FeSO_4$ selectively in the presence of Pt(IV) ions in aqueous solutions [3]. However, if more noble metal ions are present in the system, i.e. Pd(II), this kind of separation is difficult to perform due to the possibility of co-precipitation of the metals. The main reason of such behavior is the high redox potential of the noble metal ions as compared with existing reductants [4]. Hence, they are all easily reduced to the metallic form. It is still interesting however, what kind of conditions favor the reactivity of the given noble metal complex with the different reductants causing the appearance of metallic phase in the solution. One may guess that it is probably associated with the changes in chemical properties of the metal complex ions as well as with reductants used under different conditions.

The aim of our studies is to investigate kinetics and mechanism of redox reaction between the $[PtCl_6]^{2-}$ ions and $Na_2S_2O_3$. Knowing the complexing properties of thiosulfate in relation to Au(I) chloride ions [5] we chose this potential reductant with a hope for selective reduction of Pt(IV) complex to metallic form in the presence of Au(I) and Pd(II) ions. The results of our experiments are given in the next chapters. We hope, that this work will enlarge our knowledge about the processes leading to the separation of noble metals in aqueous solutions with variable pH.

2. Experimental

A. *Materials Preparation*

Starting solution of H_2PtCl_6 was prepared by dissolving of pure metallic platinum (99.99% purity, obtained from Mennica Państwowa, Warsaw, Poland) in *aqua regia*. The procedure for obtaining Pt(IV) ions in chloride system (without nitrates) was analogical to preparation of Au(III) chloride complex ions after dissolution of gold in *aqua regia*. It was described in our previous paper [6]. Obtained "base solution" was next used for the preparation of solutions with the required concentration of platinum(IV) ions. Reductant solutions were prepared by dilution of the proper amount of $Na_2S_2O_3$ crystals

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(reagent grade purity, POCh, Gliwice, Poland) in distilled water. Before experiments, each solution was buffered to adjust the proper pH. In the first part of our study, acidic solutions were chosen.

B. *Experimental Apparatus*

For kinetic studies, the Spectrophotometer (UV-2501 PC from Shimadzu, Kyoto, Japan) working in the UV-Vis range (from 190 to 900 nm) was employed. The optical path of the cuvette was 1 cm. All measurements were carried out in thermostated (±0.1°C) silica vessels. Checking for Tyndall effect in the systems after reduction reaction was conducted with simple laser apparatus (Laser He-Ne LG200 from PZO, Warsaw, Poland).

For the analysis of precipitates obtained during the studied reaction, the XRD (Miniflex II, Rigaku, Japan), XRF (Primini, Rigaku, Japan), and SEM (Scanning Electron Microscopy, Philips XL 30, Midland, Canada) techniques were applied.

C. *Experimental Procedure*

Reagents (i.e., solutions of Pt(IV) and $Na_2S_2O_3$) were rapidly mixed in the reactor (silica vessel), which was next placed as fast as possible in the compartment of a spectrophotometer. Because of relatively low rate of the studied reactions, the changes in spectrum, from 190 to 350 nm (when the solid phase doesn't precipitate) as well as from 190 to 900 nm (when the solid phases of Pt and S appeared) were registered in time. From these results, values of absorbance changes at $\lambda = 260$ nm (characteristic wavelength for $[PtCl_6]^{2-}$ ions) in time were derived. Assuming that Beer's law is valid for such a system [7], these dependencies were used for the determination of respective rate constants of reactions between platinum(IV) complexes and thiosulfate. Their values were calculated using TableCurve software [8]. All spectrophotometric experiments were repeated three times. For qualitative determination of the presence of solid particles in these systems, except for the registration of spectrum in spectrophotometer, the laser beam was passed through the samples. In case of the presence of colloidal particles in the solution, Tyndall effect was observed.

D. *Experimental Conditions*

The kinetic experiments were carried out under constant conditions of pH, temperature, different reductant concentration as well as concentration of Pt(IV) complex ions. All variants of experiments and the parameters describing experimental conditions are gathered in Tab. 1.

3. Results

A. *Thermodynamic Calculations and Model of Reaction*

It is known from the literature [9] that in a strong acid aqueous solutions containing chloride ions, platinum(IV) ions are present in the form of H_2PtCl_6, which can further dissociate to $[PtCl_6]^{2-}$ complexes. This type of ions is stable in the solution with pH $\leqslant 8$ [10].

TABLE 1

Conditions, Under Which Experiments Were Carried Out

pH	Temperature (°C)	Initial Concentration of Reductant $C_{0,\,thiosulfate}$ (M)	Initial Concentration Pt(IV) Ions $C_{0,\,Pt(IV)}$ (M)	Ionic Strength I (M)
Integral Method				
1, 3, 5, 7. 9, 12	25	$5{\cdot}10^{-3}$	$1{\cdot}10^{-4}$	0.1
Dependence of k_{obs} vs. Reductant Concentration				
1, 7	25	$1{\cdot}10^{-3}$ $2{\cdot}10^{-3}$ $3{\cdot}10^{-3}$ $4{\cdot}10^{-3}$ $5{\cdot}10^{-3}$	$1{\cdot}10^{-4}$	0.1
Initial Rate Method				
1, 7	25	50-fold excess in relation to Pt(IV) concentration	$1{\cdot}10^{-5}$ $1{\cdot}10^{-4}$ $1.9\cdot10^{-4}$ $4.9\cdot10^{-4}$	0.1
Influence of Temperature				
5, 12	5 15 25 35 45	$2.5\cdot10^{-3}$	$1\cdot10^{-4}$	0.1
Influence of Ionic Strength				
1, 7, 12	25	$5\cdot10^{-3}$	$1\cdot10^{-4}$	0.02 $NaClO_4$ 0.04 $NaClO_4$ 0.06 $NaClO_4$ 0.08 $NaClO_4$ 0.1 $NaClO_4$

In case of the sodium thiosulfate ($Na_2S_2O_3$) applied as a potential reductant, different forms of its association can be present in aqueous solution depending on pH. From predominance diagram (Fig. 1) of its dissociated products, calculated as a function of pH, it is evident that in solution with pH = 1, two forms of thiosulfate are mainly present: protonated – $H_2S_2O_3$ and partly unprotonated – $[HS_2O_3]^-$.

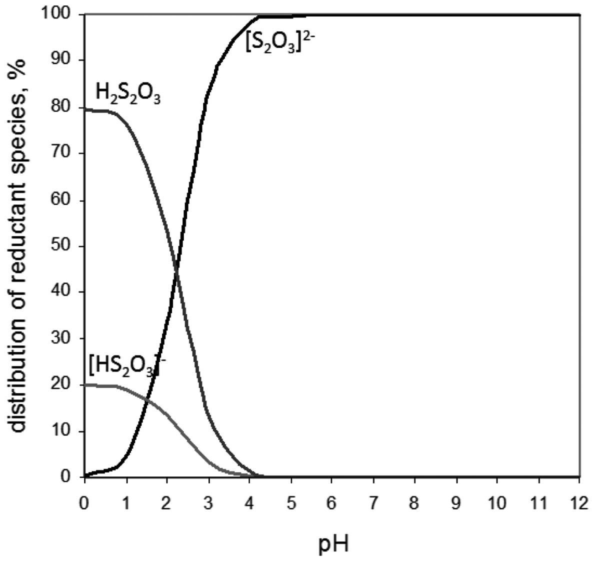

Fig. 1. Distribution of reductant species in aqueous solution calculated as a function of pH (temperature 25°C, values of dissociation constants: $K_1 = 2.51{\cdot}10^{-1}$, $K_2 = 2.51{\cdot}10^{-2}$ [11])

Having information about the forms of reagents in the initial solutions as well as the literature data about the species which can be formed during the reaction [12-20], we assumed that under experimental conditions, parallel and consecutive paths of reaction are possible during the reduction of Pt(IV) complex ions to the lower valence state. It is also likely that the metallic phase of Pt can be formed as a final product of such a process. Thus, the model of the redox reaction path can be suggested as follows:

$$Pt(IV) + [HS_2O_3]^- \xrightarrow{k_1} Pt(II) + products \tag{1}$$

$$Pt(IV) + H_2S_2O_3 \xrightarrow{k_2} Pt(II) + products \tag{2}$$

$$Pt(II) + [HS_2O_3]^- \xrightarrow{k_3} Pt(0) + products \tag{3}$$

$$Pt(II) + H_2S_2O_3 \xrightarrow{k_4} Pt(0) + products \tag{4}$$

B. *Spectrophotometric Measurements*

Spectra of solutions containing reagents have the absorption bands with maximum at λ = 260 nm (characteristic for $[PtCl_6]^{2-}$ ions) and λ 217 nm (characteristic for sodium thiosulfate). They are shown in Fig. 2.

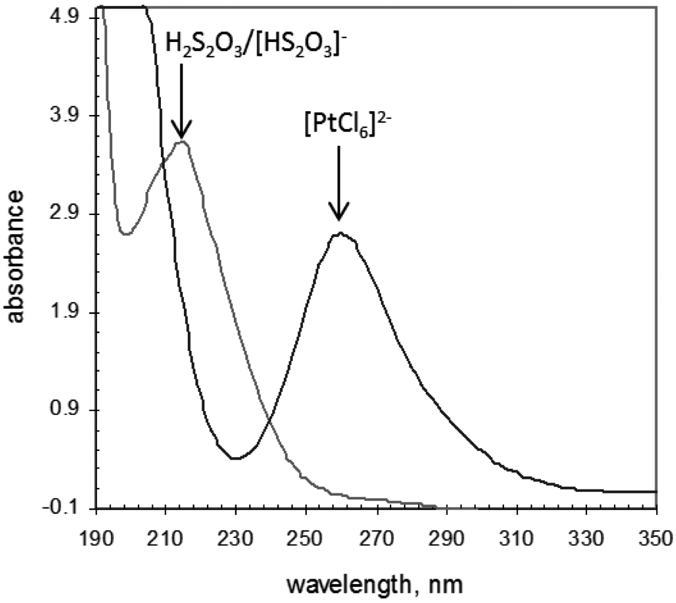

Fig. 2. Absorption bands of $[PtCl_6]^{2-}$ ions and sodium thiosulfate in aqueous solutions. Conditions: pH = 1, temperature 25°C

After mixing of reactants, disappearance of those bands was registered. It is evidence that the reaction between both reactants takes place. Additionally, in acidic solution, new absorption band appears with the maximum at λ_{max} = 238 nm (Fig. 3) during the reaction.

We are not sure what kind of a compound may correspond to this absorption band. However, because of the presence of two isosbestic points (at λ = 215 and 250 nm) in the spectrum situated at the neighborhood of the bands of reactants (Fig. 3), the presence of a compound being in equilibrium with $[PtCl_6]^{2-}$ can be suggested. Probably, it is either the thiosulfate complex of Pt(IV) or the product of Pt(IV) complex ions reduction (i.e. $[PtCl_4]^{2-}$). The chloride-thiosulfate complex of platinum(IV) can be formed by the substitution of Cl^- ligand in octahedral platinum(IV) complex ion, e.g.:

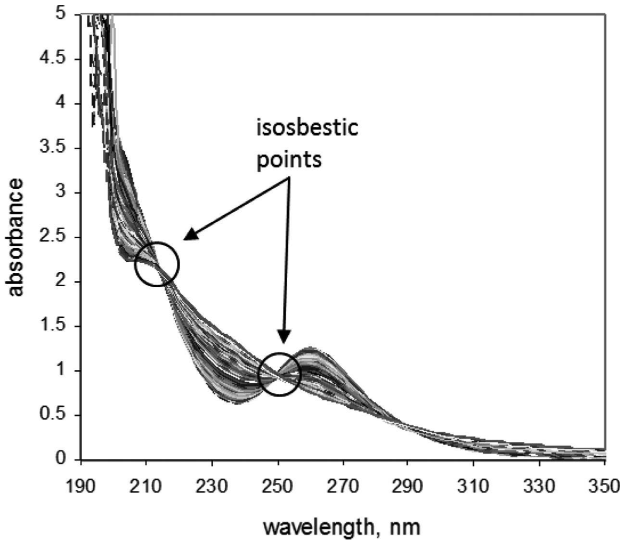

Fig. 3. Absorption bands of $[PtCl_6]^{2-}$ ions and sodium thiosulfate in aqueous solutions after mixing of these solutions. Conditions: pH = 1, temperature 25°C

$$[\overset{+4}{Pt}Cl_6]^{2-} + [HS_2O_3]^-/H_2S_2O_3 \xrightarrow{k_1(k_2)} [\overset{4+}{Pt}Cl_4(S_2O_3)]^{2-} + H^+/2H^+ + 2Cl^- \tag{5}$$

It is also very likely that the absorbance band with maximum at λ = 238 nm belongs to $[PtCl_4]^{2-}$. This suggestion may be concluded from the comparison of the registered spectra with those obtained for another redox systems in which $[PtCl_6]^{2-}$ ions were reduced by ethyl alcohol and L-ascorbic acid [21]. In both cases the absorption band at λ = 238 nm was also present. Thus, the possible presence of the $[PtCl_4(S_2O_3)_2]^{2-}$ formation as an intermediate step prior the appearance of $[PtCl_4]^{2-}$ in the system:

$$[\overset{4+}{Pt}Cl_4(S_2O_3)]^{2-} + H_2O \xrightarrow{k_3} [\overset{2+}{Pt}Cl_4]^{2-} + SO_4^{2-} + 2H^+ + S\downarrow \tag{6}$$

suggests the more complex mechanism of the studied reaction.

C. *Molecularity of Elementary Reaction*

In order to determine the molecularity of the first stage of the studied reaction, the integral method was used. In these experiments, large amount of reductant (20-fold higher than concentration of Pt(IV) complex ions) was applied. In such a case, differential rate equation for the reaction (2) and (3) is following:

$$-\frac{dC_{Pt(IV)}}{dt} = k_{obs}C^n_{Pt(IV)} \tag{7}$$

where:

$$k_{obs} = k_1C_{[HS_2O_3]^-} + k_2C_{H_2S_2O_3} \tag{8}$$

n – the order of reaction in respect to Pt(IV) complex ions (it was assumed that for the reductant$n$ = 1).

Data analysis consisted of the subsequent substitution of n in eq. (7) by the numbers 0.5, 1, 1.5, 2 and 3. Obtained differential equations were analytically solved, giving their adequate integral forms. Finally, experimentally obtained kinetic data ($Abs \sim C_{Pt(IV)} = f(t)$) were recalculated and redrawn as linear dependences with accordance to these integral equations (graphical procedure). For all experiments obtained in the solution with pH = 1 the approach with $n = 1$ gave the linear dependence in the $\ln C_{Pt(IV)}$ = f(t) system and strongly suggests first-order kinetics of the reaction. Further fitting procedure, carried out using TCCurve software, confirmed the suggested kinetics, giving the form of equation:

$$Abs(\propto C_{[PtCl_6]^{2-}}) = a\exp(-bt) \tag{9}$$

The a and b parameters in eq. (9) correspond to the $Abs_0 \sim C_{0,Pt(IV)}$ and the observed rate constant (k_{obs}), respectively. Taking into account two forms of reductant as well as the large excess of reductant (pseudo-first-order conditions) it can be suggested, that in both cases, a process of $[PtCl_6]^{2-}$ reduction takes place via two parallel paths, and each of them can be described as bimolecular reaction. It can be the confirmation of the mechanism described with equations (2) and (3).

D. *Effect of Reductant Concentration on the Rate Constant*

Convenient test enabling to suggest a mechanism of the reaction is based on a dependence of the reductant concentration vs. rate constant. Consequently, the measurements with increasing amount of the reductant in the solution with pH = 1, were carried out. Obtained values of the rate constants are gathered in Table 2.

TABLE 2

Values of the Rate Constant of $[PtCl_6]^{2-}$ Reaction with Sodium Thiosulfate at Different Concentration of Reductants. Conditions: pH = 1, $C_{0,[PtCl_6]^{2-}} = 1{\cdot}10^{-4}$ M, Temperature = (25±0.1)°C, Ionic Strength = 0.1 M $NaClO_4$

Concentration of Reductant $C_{reductant}$ (M)	The Rate Constant k_{obs} (Average of Four Experiments) (s^{-1})	Mean Standard Deviation σ (s^{-1})
$1 \cdot 10^{-3}$	0.00061	0.00002
$2 \cdot 10^{-3}$	0.00092	0.00001
$3 \cdot 10^{-3}$	0.00100	0.00001
$4 \cdot 10^{-3}$	0.00133	0.00003
$5 \cdot 10^{-3}$	0.00180	0.00007

According to the equation (8), k_{obs} should be proportional to the concentration of reductant ($C_{reductant}$) if the reaction either (4) or (5) is valid. Our results (Fig. 4) show that this condition is fulfilled for pH = 1.

However, extrapolation of this dependence to the "zero concentration" of reductant yields an intercept with the k'' value at Y axis, (Fig. 4). The empirical equation describing k_{obs} vs. reductant concentration has the form:

$$k_{obs} = 0.2793 \cdot C_{reductant} + k'' \tag{10}$$

After substitution of equation (10) into (7) (assumption: $n = 1$) a new form of the rate equation for Pt(IV) ions can be obtained:

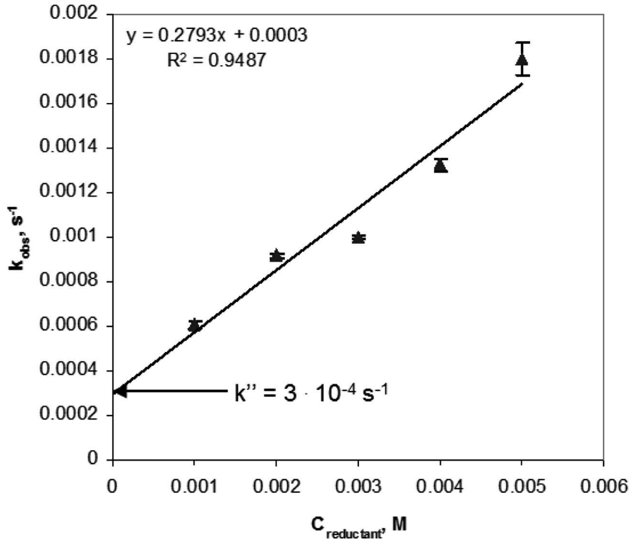

Fig. 4. Dependence of the k_{obs} vs. $C_{reductant}$ for the reaction of $[PtCl_6]^{2-}$ ions with sodium thiosulfate. Conditions: pH = 1, $C_{0,[PtCl_6]^{2-}} = \cdot\ 10^{-4}$ M, temperature 25°C

$$-\frac{dC_{Pt(IV)}}{dt} = k' \cdot C_{reductant} C_{Pt(IV)} + k'' C_{Pt(IV)} \tag{11}$$

where, $k' = 0.2793 s^{-1}$. Equation (11) suggests that simultaneously with the reduction of $[PtCl_6]^{2-}$ ions, they can also disappear in parallel reaction with the rate constant k'':

$$[PtCl_6]^{2-} \xrightarrow{k''} products \tag{12}$$

E. *Effect of Ionic Strength*

The useful part of our studies consisted in the determination of the influence of ionic strength (I) on the rate of $[PtCl_6]^{2-}$ ions reduction. This kind of experiments gave the information about charges of reacting species and can help to suggest the mechanism of the reaction (the methodology and the interpretation of the salt effect in the other redox system was described in [21]). All experiments were carried out at pH = 1, for different I, changed from 0.02 to 0.1 M. The obtained values of the rate constants are gathered in Table 3.

TABLE 3

Values of the Rate Constant of $[PtCl_6]^{2-}$ Reaction with Sodium Thiosulfate at Different Ionic Strength. Conditions: pH = 1, $C_{[PtCl_6]^{2-}} = 1 \cdot 10^{-4}$ M, temperature = (25 ±0.1)°C

Ionic Strength I (M)	The Rate Constant $k_{obs,1}$ (Average of Four Experiments) (s^{-1})	Mean Standard Deviation σ (s^{-1})
0.02	0.00200	0.00006
0,04	0.00214	0.00002
0,06	0.00242	0.00010
0,08	0.00264	0.00002
0,10	0.00299	0.00005

According to the Brönstedt-Bjerrum (B-B) equation:

$$\log\left(\frac{k_{obs}}{k_{0,obs}}\right) = 2z_A z_B A\left(\frac{\sqrt{I}}{1+\sqrt{I}}\right) \tag{13}$$

where z_A, z_B are the charges of reagents and A is the constant value for aqueous solution (A = 0.509). It can be clearly seen, that for the same charges of reacting species, the reaction should be accelerated. The graphical form of experimentally obtained results is illustrated in Fig. 5 and shows that an increase of the ionic strength yields an increase of the rate constant.

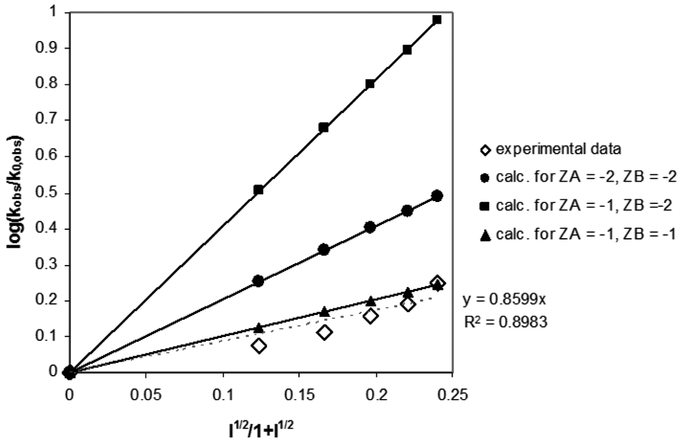

Fig. 5. Salt effect in the redox reaction between $[PtCl_6]^{2-}$ ions and sodium thiosulfate according to Brönstedt-Bjerrum dependence – $\log(k_{obs}/k_{0,obs})$ vs. $I^{1/2}/(1+I^{1/2})$. Conditions: pH = 1, temperature 25°C

Comparing the calculated and experimental results (Fig. 5) it can be assumed that in the studied system charges of reacting species are close to "–1". Therefore, possibility of the reaction between the dissociated form of reductant ($[HS_2O_3]^-$) as well as Pt(IV) complex ion, cannot be excluded. Consequently, in order to accept that the product $z_{[HS_2O_3]^-} z_{Pt(IV)} = 1$, complex ion of Pt(IV) should coordinate only five chloride (or hydroxyl) ions. Hence, the reduction reaction of Pt(IV) in acidic solution (pH = 1) can be the following:

$$[PtCl_5]^- + [HS_2O_3]^- \xrightarrow{k} [PtCl_4]^{2-} + S\downarrow + SO_3 + Cl^- + H^+ \tag{14}$$

However, the identification of $[PtCl_5]^-$ intermediates should be done using more advanced experimental techniques (e.g., described in [22]) than those employed in this study.

F. *The Order of Reaction*

To determine an order of the studied reaction with respect to $[PtCl_6]^{2-}$ ions, a method of the initial rate was applied. The rate constant of reaction at the initial time of Pt(IV) reduction process for four different initial concentration of $[PtCl_6]^{2-}$ ions was measured. Values of the obtained rate constants are gathered in Table 4.

Assuming that the rate equation (of $[PtCl_6]^{2-}$ ions reduction) has the form of eq. (7), it can be suggested that in the initial period of time of the studied reaction, the rate of reduction process (v_0) is described by equation:

$$v_0 = k_{obs} C^n_{[PtCl_6]^{2-}} \tag{15}$$

TABLE 4

Values of the Rate Constant of $[PtCl_6]^{2-}$ Reaction with Sodium Thiosulfate at Different Initial Concentration of Platinum(IV) Complexes. Conditions: $C_{0,Na_2S_2O_3} = 5\cdot10^{-3}$ M, pH = 1, temperature = (25±0.1)°C, Ionic Strength = 0.1 M $NaClO_4$

Initial Concentration of $[PtCl_6]^{2-}$ $C_{reductant}$ (M)	The Rate Constant k_{obs} (Average of Four Experiments) (s^{-1})	Mean Standard Deviation σ (s^{-1})
$5\cdot10^{-5}$	0.01445	0.00201
$1\cdot10^{-4}$	0.01307	0.00180
$1.9\cdot10^{-4}$	0.00175	0.00013
$4.9\cdot10^{-4}$	0.000078	0.000001

Taking the logarithm of both sides of equation (15), a linear dependence should be obtained:

$$\log v_0 = \log k_{obs} + n\log C_{0,[PtCl_6]^{2-}} \tag{16}$$

The slope (n) of the obtained dependence defines the order of the studied reaction with respect to $[PtCl_6]^{2-}$ species. Experimentally obtained results (for pH = 1), are shown in Fig. 6. It can be seen that in case of Pt(IV) reduction, $\log v_0$ vs. $C_{0,[PtCl_6]^{2-}}$ the dependence was found to be non–linear. It can be suggested that in this environment, a mechanism of the reaction is complex and determination of the order by the initial rate method is not possible.

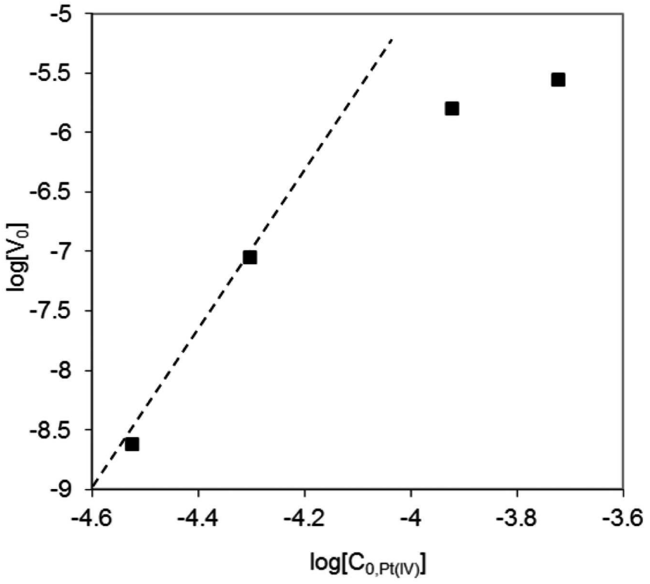

Fig. 6. Dependence of $\log(v_0)$ vs. $\log(C_{0,Pt(IV)})$ for the reaction reduction of $[PtCl_6]^{2-}$ with sodium thiosulfate. Conditions: pH = 1, temperature 25°C

G. *Effect of pH*

In order to determine the influence of acidity on the kinetics of $[PtCl_6]^{2-}$ reduction, experiments were carried out at different pH = 1.05, 3.29, 5.02. The constant value of pH was adjusted using respective buffer solutions[1].

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[1] Britton-Robinson and Clark-Labes buffer solutions [11].

Spectral analysis of the reacting system in the solutions with pH = 1-3 (Fig. 7) showed that during the $[PtCl_6]^{2-}$ reduction with sodium thiosulfate, intensive bands in the range of the visible spectrum (350-900 nm) are present. Such bands are characteristic for the colloidal form of the solid phase. During the reaction, two additional absorption bands can be observed. First, at λ = 280 nm, which is characteristic for $SO_2 \cdot H_2O$ solutions and the second one at λ = 380 nm, which we cannot identify. It may be the solid colloidal phase of Pt.

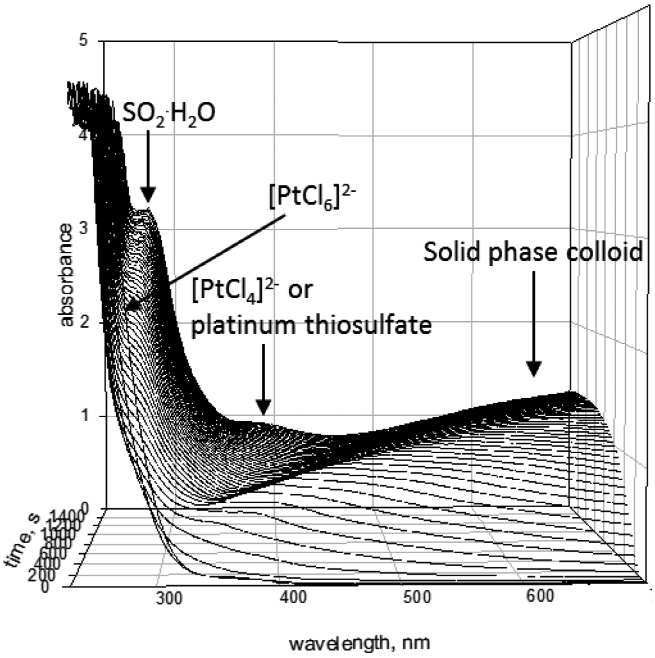

Fig. 7. Spectra of the aqueous solution during the reaction of $[PtCl_6]^{2-}$ ions with sodium thiosulfate, with characteristic absorption bands in the range from 200 to 700 nm. Conditions: pH = 1, $C_{0,[PtCl_6]^{2-}} = 1 \cdot 10^{-4}$ M, temperature 25°C

The presence of the colloidal phase was also detected using laser beam technique. It allows us to demonstrate the presence of Tyndall effect in the studied system. Also, the change in color of the solution from the milky throughout yellow, orange and brown to the black one was observed. The same behavior of the system was described by Trzebiatowski [24] for transformation of the silver (and other heavy metals) thiosulfate compounds into the Ag_2S precipitate. Thus, one can suggest that analogically to those systems, thiosulfate platinum(II) complexes and finally platinum sulfide (PtS) can be formed:

$$[PtCl_4]^{2-} + H_2S_2O_3/[HS_2O_3]^- \rightarrow Pt(S_2O_3) + 2H^+/H^+ + 4Cl^- \tag{17}$$

$$Pt(S_2O_3) + H_2O \xrightarrow{k} PtS \downarrow + H_2SO_4 \tag{18}$$

This type of platinum sulfide is in agreement with thermodynamic data [24]. Considering the stability of platinum sulfides (PtS and PtS_2) in the reaction system:

$$Pt + S = PtS \Delta G^o_{298} = -156.7[J/mol] \tag{19}$$

$$Pt + 2S = PtS_2 \Delta G^o_{298} = -256.5[J/mol] \tag{20}$$

one can conclude that the PtS_2 is more stable. However, the PtS being less stable compound will appear first in the solution. The presence of PtS was confirmed by XRD and SEM studies (see sec. H). The platinum sulfide formation (eq. 18) can be preceded by the step of electron transfer from the sulfur atom in thiosulfate ligand causing the metallic Pt formation (results of SEM and XRD studies) in the system:

$$Pt(S_2O_3) + H_2O \xrightarrow{k} Pt \downarrow + S \downarrow + H_2SO_4 \tag{21}$$

Of course, one cannot exclude $Na_2S_2O_3$ decomposition in acidic solution:

$$Na_2S_2O_3 \rightarrow SO_2 \cdot H_2O + S \downarrow \tag{22}$$

These observations allow us to suggest that in the pH range from 1 and 3, parallel processes described by the reaction (18), (19), (21) and (22) could occur in the system.

It was also found that in the solution with pH = 5, the milky colloid is not present. Only black precipitate has appeared during the reaction.

H. *SEM and XRD analysis*

Black precipitate, which was a final product of the Pt(IV) ions reduction, was analyzed using SEM, XRD and XRF techniques. Comparison of the obtained spectrum with that characteristic for sulfur, pure platinum and platinum sulfides (PtS and PtS_2) confirm the presence of sulfur (Fig. 8a and 8b) and also strongly suggest the presence of Pt (Fig. 8a) and PtS (Fig. 8b). The presence of metallic phase of Pt was also confirmed by XRF analysis.

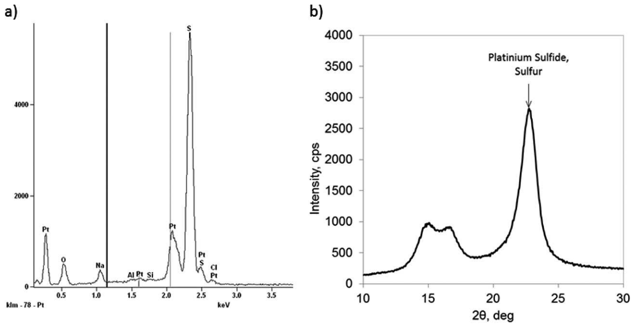

Fig. 8. SEM – a) and XRD – b) analysis of the colloidal precipitate obtained in the reaction of $[PtCl_6]^{2-}$ with sodium thiosulfate in aqueous solution at pH = 1

I. *Effect of Temperature*

Because of the colloidal sulfur formation in the solution with pH = 1 and pH = 3, the temperature dependence in these systems was not determined. Influence of temperature on the kinetics of redox reaction between $[PtCl_6]^{2-}$ and sodium thiosulfate was studied in the solution with pH = 5, in the range from 5 to 45°C. Obtained values of the rate constants are gathered in Table 5.

Results show that the rate constant of $[PtCl_6]^{2-}$ reduction reaction increase with the increase of temperature. Determined rate constants were used to calculate enthalpy (ΔH^*) and entropy (ΔS^*) of activation for the studied reaction. Applying graphical method, from the logarithmic form of Eyring equation (23):

TABLE 5
The observed rate constant of the reduction reaction of $[PtCl_6]^{2-}$ with sodium thiosulfate obtained at different temperatures

Temperature (K)	Rate Constant (Average of Four Experiments), $k\cdot 10^3$ (s^{-1})	Mean Standard Deviation (σ) (s^{-1})
	pH = 5	
278	1.04	0.10
288	1.43	0.13
298	2.31	0.15
308	3.83	0.21
318	8.87	0.52

$$\ln\frac{k}{T} = 46.786 + \frac{\Delta S^*}{R} - \frac{\Delta H^*}{R}\cdot\frac{1}{T} \tag{23}$$

the values of these parameters were calculated. They are gathered in the Table 6.

TABLE 6
The Parameters in Eyring Equation for the Reaction of $[PtCl_6]^{2-}$ Ions with Sodium Thiosulfate

pH	$46.786 + \Delta S^*/R$	$\Delta H^*/R$	Enthalpy of Activation ΔH^* (kJ · mol^{-1})	Entropy of Activation ΔS^* (J · mol^{-1}· K^{-1})
5	9.787	4320	35.91	-307.6

4. Disscusion and conclusions

Having the knowledge of complexing properties of thiosulfate in relation to metal ions, as well as their potential reducing properties, e.g. for Au(I) ions [22], we used $Na_2S_2O_3$ with a hope to find selective reductant of Pt(IV) chloride complex ions to metallic form.

Experimentally obtained kinetic data, described in this paper, enable us to discuss the possible mechanism of the studied reaction. Determined molecularity of the first elementary step of platinum(IV) complex ions reduction as well as the fit of the rate equation form (eq. 9) to the obtained kinetic curves suggest that the reduction reaction of $[PtCl_6]^{2-}$ ions has a pseudo-first order character. However, since both reactant and reductant species depend strongly on pH, different mechanisms of this reaction are possible. Taking into account a distribution of reductant species as a function of pH (Fig. 1), in acidic solution (pH = 1) the parallel paths of the reactions can be present in the studied system. In such a case two forms of the reductant can react with the $[PtCl_6]^{2-}$ ions. The parallel paths of the reaction can be also suggested from the dependence k_{obs}vs. $C_{reductant}$ (Fig. 4) by the presence of an interception of the Y axis, which changes the formula of observed rate constant (eq. 10). This suggests a disappearance of the Pt(IV) ions with the rate constant k'' (eq. 12). Taking into account an equilibrium composition of reductant solution under experimental conditions (pH = 1), it is very likely that two different forms of the reductant ($H_2S_2O_3$ and $[HS_2O_3]^-$) can take part in the reaction. In fact, because of the large excess of reductant as compared to Pt(IV) concentration used in experiments, k" can be a cumulated rate constant, which include one of the form of the reductant:

$$k'' = k_2 \cdot C_{[HS_2O_3]^-} \tag{24}$$

Substitution of equation (24) into (11) gives a new formula of the empirically obtained rate equation:

$$-\frac{dC_{Pt(IV)}}{dt} = k_1 \cdot C_{H_2S_2O_3}C^n_{Pt(IV)} + k_2 \cdot C_{[HS_2O_3]^-}C^n_{Pt(IV)} \tag{25}$$

If one assumes that $n = 1$, the equation (25) is in agreement with formula (10) which was obtained from the fitting procedure.

From the above discussion one can conclude, that mechanism of the $[PtCl_6]^{2-}$ reaction in the solution with pH = 1 is complex, and consists in two parallel paths, with two forms of reductant ($H_2S_2O_3$, $[HS_2O_3]^-$) taking part in the reaction. Analyzing experimental data we can suggest that sodium thiosulfate is a reductant of $[PtCl_6]^{2-}$ ions. The reduction leads to the $[PtCl_4]^{2-}$ formation (eq. 6) and finally to the Pt precipitation (eq. 21) via the intermediate platinum(IV)-thiosulfate (eq. 5) and platinum(II)-thiosulfate (eq. 20) complex formation in the system. Parallel, as a result of the $Pt(S_2O_3)$ and sodium thiosulfate decomposition (eq. 18 and eq. 22) in acidic solutions (pH from 1 to 3), the PtS and sulfur particles are formed, respectively. The mechanism of platinum sulfide formation can be also described by eq. 19. The presence of Pt, PtS as well as S in the precipitate was confirmed from the SEM, XRD and XRF studies.

Consequently, the mixture of such colloidal particles appears in the system giving the unambiguous composition, difficult to analyze using SEM and XRD methods. Summarizing the above discussion it can be concluded that:

- Black precipitate can be obtained in acidic solutions (pH from 1 to 5). It is a mixture of Pt, sulfur and PtS colloids.
- The suggested mechanism of the reduction in acidic solutions (pH from 1 to 5) can be following:

I stage:

$$[\overset{+4}{Pt}Cl_6]^{2-} + [HS_2O_3]^-(H_2S_2O_3) \xrightarrow{k_1(k_2)} [\overset{4+}{Pt}Cl_4(S_2O_3)]^{2-} + H^+(2H^+) + 2Cl^-$$

$$[\overset{4+}{Pt}Cl_4(S_2O_3)]^{2-} + H_2O \xrightarrow{k_3} [\overset{2+}{Pt}Cl_4]^{2-} + S\downarrow + SO_4^{2-} + 2H^+$$

II stage:

$$[\overset{2+}{Pt}Cl_4]^{2-} + [HS_2O_3]^-(H_2S_2O_3) \xrightarrow{k_4(k_5)} \overset{2+}{Pt}(S_2O_3) + H^+(2H^+) + 4Cl^-$$

$$Pt(S_2O_3) + H_2O \xrightarrow{k_6} Pt\downarrow + S\downarrow + SO_4^{2-} + 2H^+$$

$$Pt + S \xrightarrow{k_8} PtS\downarrow$$

$$Pt(S_2O_3) + H_2O \xrightarrow{k_7} PtS\downarrow + SO_4^{2-} + 2H^+$$

- The best conditions for the precipitation of Pt colloid seems to be pH = 5. Under these conditions insignificant amount of colloidal sulfur appears in the system.
- The rate equation for the reduction reaction of $[PtCl_6]^{2-}$ at pH = 5 can be expressed as:

$$C_{[PtCl_6]^{2-}} = C_{0,[PtCl_6]^{2-}} \exp\left(-Te^{\left(9.787-4.320\frac{1}{T}\right)} \cdot t\right)$$

where, $C_{0,[PtCl_6]^{2-}}$is the initial concentration of $[PtCl_6]^{2-}$, t – time, T – temperature in Kelvin.

- The method of reduction of $[PtCl_6]^{2-}$ ions using sodium thiosulfate can be used for the precipitation of Pt species from aqueous chloride solution. However, the pure product of Pt cannot be obtained.

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