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KINETIC STUDIES OF Pt(IV) CHLORIDE COMPLEX IONS REDUCTION REACTION USING POTASSIUM FORMATE

In this paper, the kinetics of the platinum(IV) chloride complex ions reduction reaction was studied. It was shown that the mechanism exhibits autocatalytic character. The presence of metallic platinum in the system significantly increases the reaction rate. The influence of the initial concentration of precursor, reductant, ionic strength, initial concentration of the chloride ions as well as the temperature on the process rate was investigated. The activation energy was determined and is equal to 93.57 kJ/mol. Moreover, the obtained metallic phase was analyzed, and it was observed that it has a micrometric size.

Keywords: platinum, recovery, recycling, activation energy, reaction mechanism

1. Introduction

Platinum belongs to the group of precious metals. Its unique chemical and physical properties mean that the price of this metal increases every year. For this reason, the recycling of this metal is economically justified. Depending on the use of platinum, the recycling process must be tailored to the waste.

It is obvious that the recovery of platinum from ceramic catalysts (*e.g.* automotive) will be carried out in a different way compared to the process of recycling of this metal from the petrochemical or chemical industry. Regardless of what source the waste comes from, in most of cases, hydrometallurgical processes are used. This is mainly due to the fact that the melting point of platinum is very high (1768°C). In addition, due to the large dispersion of valuable metal in catalysts, the use of pyrometallurgical methods could be associated with large platinum losses.

The main advantage of hydrometallurgical methods is the low price of the solvent. Additionally, water purification processes are much cheaper than organic solvents.

The chemical properties of platinum also impose some restrictions. Platinum, as a noble metal, is practically insoluble in mineral acids [1]. It dissolves relatively quickly only in aqua regia. During dissolving of platinum in aqua regia, the platinum ions form chloride complexes [2]. These complexes are stable,

however their structure strongly depends on pH of the solution as well as chloride ion concentration.

Potassium cyanide is another reactant, which is commonly used for platinum dissolution [3,4]. This method however, raises some emotions among the society [5], mainly due to the awareness of the high toxicity of potassium and hydrogen cyanide. For this reason, small recycling companies are reluctant to use this reagent, despite its significant advantages. Even large plants, such as KGHM Polska Miedź, which process about 93 kg (in 2018) of platinum and palladium annually, uses chloride solutions [6].

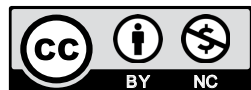
In the case of application of chloride solutions for platinum recycling and refining, the problem of platinum precipitation appears at the end of the process [7]. Theoretically, platinum can be recovered from chloride solutions using electrolysis process, but this leads to the evolution of chlorine gas at the anode. This process is strongly undesirable, mainly due to the toxicity of this gas as well as its corrosive properties. Therefore, frequently platinum complex ions are reduced to metallic form by other means. For example, it was shown, that the adsorption of Pt(IV) chloride complexes at activated carbon surface leads to its reduction to Pt(II) and then to Pt(0) [8-10]. Also other reductants can be used for example: vitamin C [11,12], NaBH₄ [13,14], formaldehyde [15], hydrogen [16], methanol [17].

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In this paper, the kinetic studies about platinum recovery from acidic chloride solution using potassium formate is described.

2. Experimental

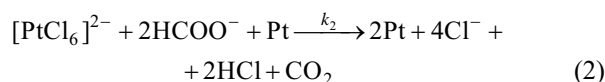
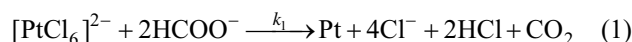
In the experiment deionized water (conductivity <math><0.07\text{ S/cm}</math>) obtained using Hydrolab HLP-30) deionizer with impurities' concentrations: Na^+ , SO_4^{2-} , Cl^- , Br^- , NO_2^- , NO_3^- , PO_4^{3-} <math><0.5\text{ ppb}</math>; Fe, Zn, Cu, Cr, Mn <math><0.1\text{ ppb}</math>; was used. If not mentioned, all chemical reagents were of analytical purity. As the reductant, the aqueous solution of potassium formate was used. Platinum(IV) chloride complex ions were obtained according to the methodology described in our previous paper [8]. The ionic strength was set up using sodium perchlorate. The introduction of additional cation to the system was dictated by the low solubility of potassium perchlorate salt. The initial concentration of chloride ions was controlled by the addition of potassium chloride. All kinetics measurements were performed using a UV-Vis spectrophotometer (Shimadzu model U-2501PC). The pH of the solution was controlled by the addition of sodium hydroxide and perchloric acid (both reagents were purchased from POCH).

3. Results and discussion

All experiments were carried out at an elevated temperature since at room temperature, the reaction was very slow. If not specified else, the chloride ions concentration was proportional to the concentration of [Pt(IV)], the pH of the solution was equal

to 4. In Fig. 1A the evolution of the UV-Vis spectra with time are shown. These are caused by Pt(IV) chloride complex ions reduction. The exemplary kinetic curve of this process is shown in Fig. 1B. It has to be underlined, that the peak shape as well as position corresponds probably to the $[\text{PtCl}_6]^{2-}$ [9,10].

As it can be seen, the kinetic curve has a specific sigmoidal shape. This suggests that the studied process has an autocatalytic character. Therefore, the following scheme of the studied reaction is proposed:



In the case of a significant excess of the reductant, the changes in its concentration can be neglected. Therefore the following assumption was adopted:

$$k_{1,obs} = k_1 \cdot [\text{HCOO}^-]_0 \quad (3)$$

$$k_{2,obs} = k_2 \cdot [\text{HCOO}^-]_0 \quad (4)$$

where k_1 , k_2 , $k_{1,obs}$, $k_{2,obs}$ are the rate constants and the observed rate constants for both reactions, whereas $[\text{HCOO}^-]_0$ stands for formate initial concentration.

Taking into account the eq. (1), (2), (3) and (4), the following differential equation system can be given:

$$\begin{cases} \frac{d[\text{PtCl}_6^{2-}]}{dt} = -k_{1,obs} \cdot [\text{PtCl}_6^{2-}] \\ \frac{d[\text{PtCl}_6^{2-}]}{dt} = -k_{2,obs} \cdot [\text{Pt}^0] [\text{PtCl}_6^{2-}] \end{cases} \quad (5)$$

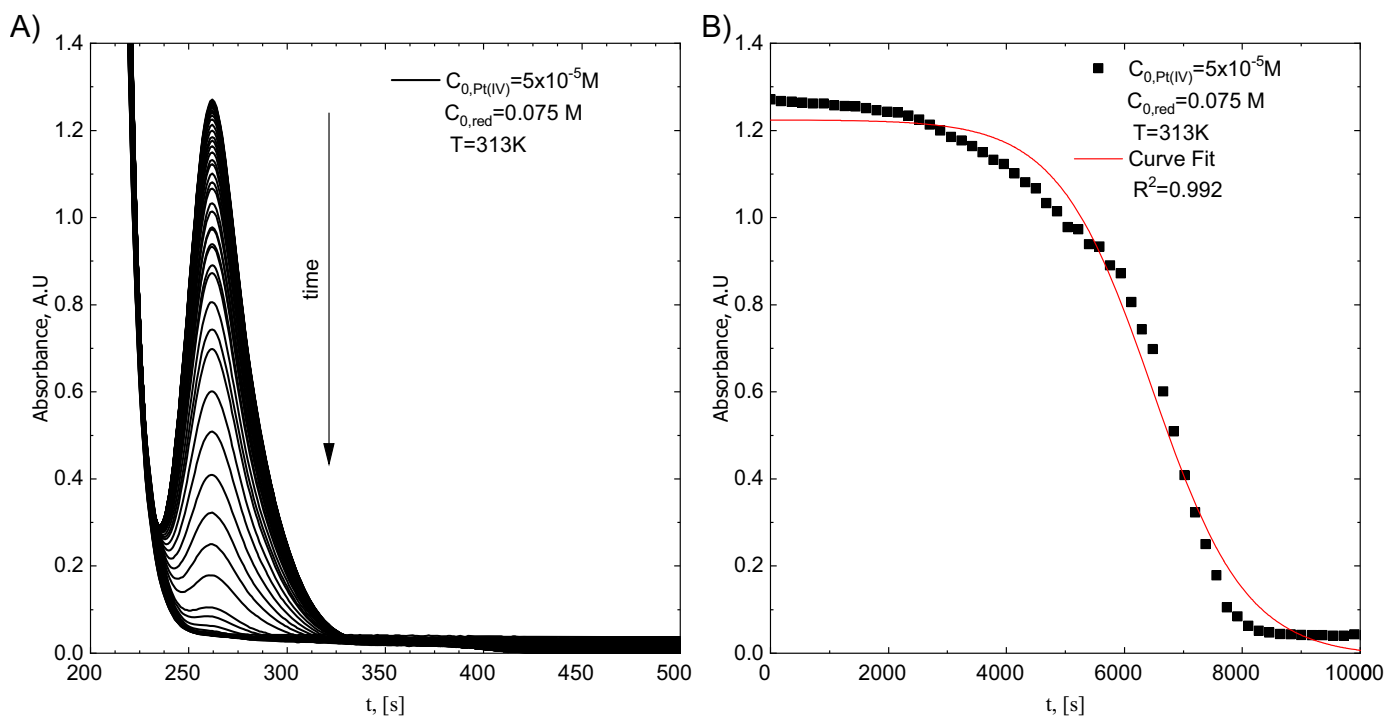


Fig. 1. Evolution of UV-Vis spectra during the reduction reaction A), absorbance at the maximum of the Pt(IV) complex ions absorption band as a function of time, platinum and potassium formate initial concentrations, $C_{0,\text{Pt(IV)}}$ and $C_{0,\text{red}}$ respectively are given in the figure

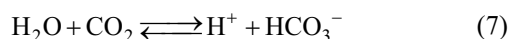
The solution of this equation system can be given in the following form:

$$[\text{PtCl}_6^{2-}] = \frac{[\text{PtCl}_6^{2-}]_0 + \frac{k_{1,obs}}{k_{2,obs}}}{1 + \frac{k_{1,obs}}{k_{2,obs}[\text{PtCl}_6^{2-}]_0}} \exp\left\{\left(\frac{k_{1,obs}}{k_{2,obs}} + [\text{PtCl}_6^{2-}]_0\right)k_{2,obs}t\right\} \quad (6)$$

where $[\text{PtCl}_6^{2-}]_0$ is the initial concentration of Pt(IV) complex ions.

The aforementioned equation was used to fit the kinetic curve and determine the observed rate constants as shown in Fig. 1B.

It should be mentioned that during the experiments, there was no evolution of gaseous products. This is probably due to high carbon dioxide solubility in water, about 0.9 dm³ in 1 dm³ at the room temperature and atmospheric pressure. Only *ca.* 0.1% of dissolved CO₂ forms weak carbonic acid according to eq. (7).



3.1. The influence of the reductant initial concentration on the reaction rate

In Fig. 2 the influence of the reductant initial concentration on the observed rate constants is shown. It can be concluded that $k_{1,obs}$ is independent of the initial concentration of reductant (Fig. 2A). According to the Anova test, at the 0.05 level, the slope is not significantly different from zero. This suggests that

the reduction process is zero order with respect to the reductant concentration. In the case of $k_{2,obs}$ (see Fig. 2B), there is a clear linear correlation between reductant initial concentration and the observed rate constant. This seems to confirm that assumption given in eq. (4) is valid.

It can also be seen that the error bars are significant though the measurements were repeated 5 times. It can be explained with the fact, that in the case of the autocatalytic reaction, even a small deviation in temperature, initial concentration of reagents, as well as trace of metallic platinum at the surface of the reactor, may significantly change the process rate. For instance, when the experiments were carried out at the room temperature, the uncertainties of observed rate constants for the autocatalytic process were > 100%. They decreased as temperature increased. To avoid the errors coming from the presence of Pt particles on the surface of spectrophotometric curvettes, they were cleaned after each experiment using boiling aqua regia.

3.2. The influence of the Pt(IV) chloride complex ions initial concentration on the reaction rate

In Fig. 3A and B the influence of Pt(IV) chloride complex ions initial concentration on the observed rate constants $k_{1,obs}$ and $k_{2,obs}$ is given.

Again, it can be seen, that error bars are significant. Despite this fact, the linear correlation between Pt(IV) initial concentration and $k_{2,obs}$ can be observed. This confirms that the second step of the reaction is first order with respect to the Pt(IV) initial concentration, according to the eq. (5). In the case of $k_{1,obs}$ at the 0.05 level, the slope is not significantly different from zero. This standard error was scaled with square root of reduced Chi-Sqr. This suggest, that the first step of the reaction is 0 order.

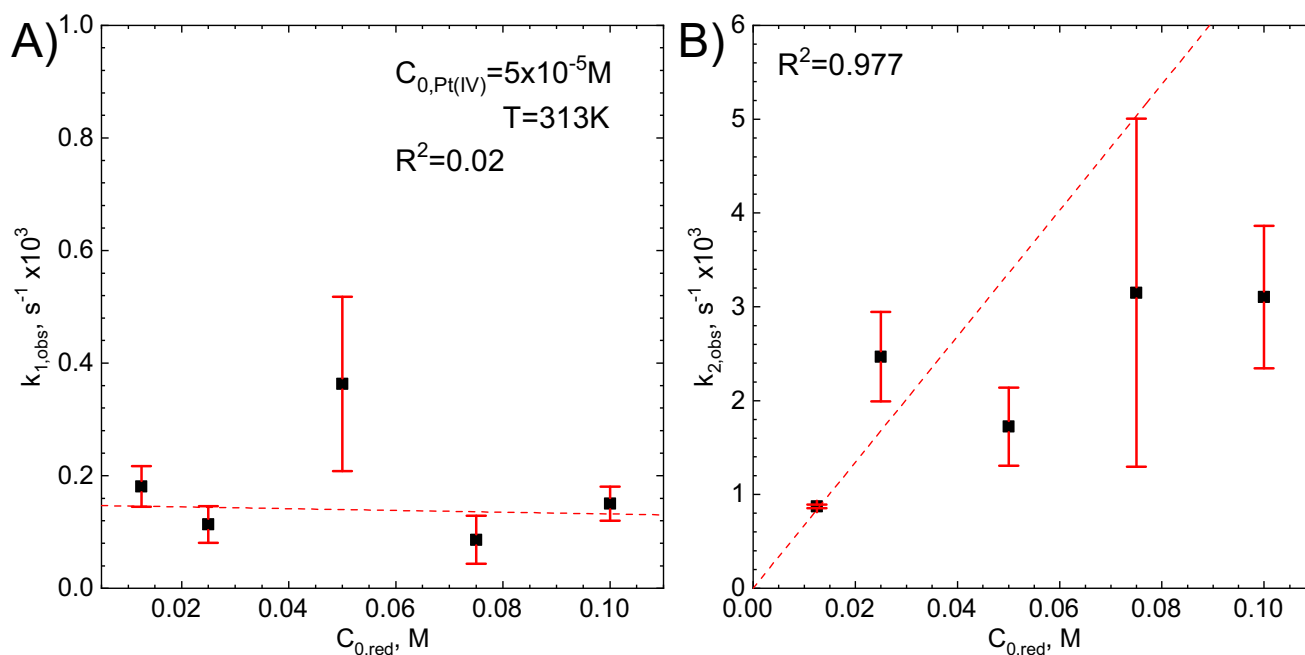


Fig. 2. The influence of the reductant initial concentration on the observed rate constants

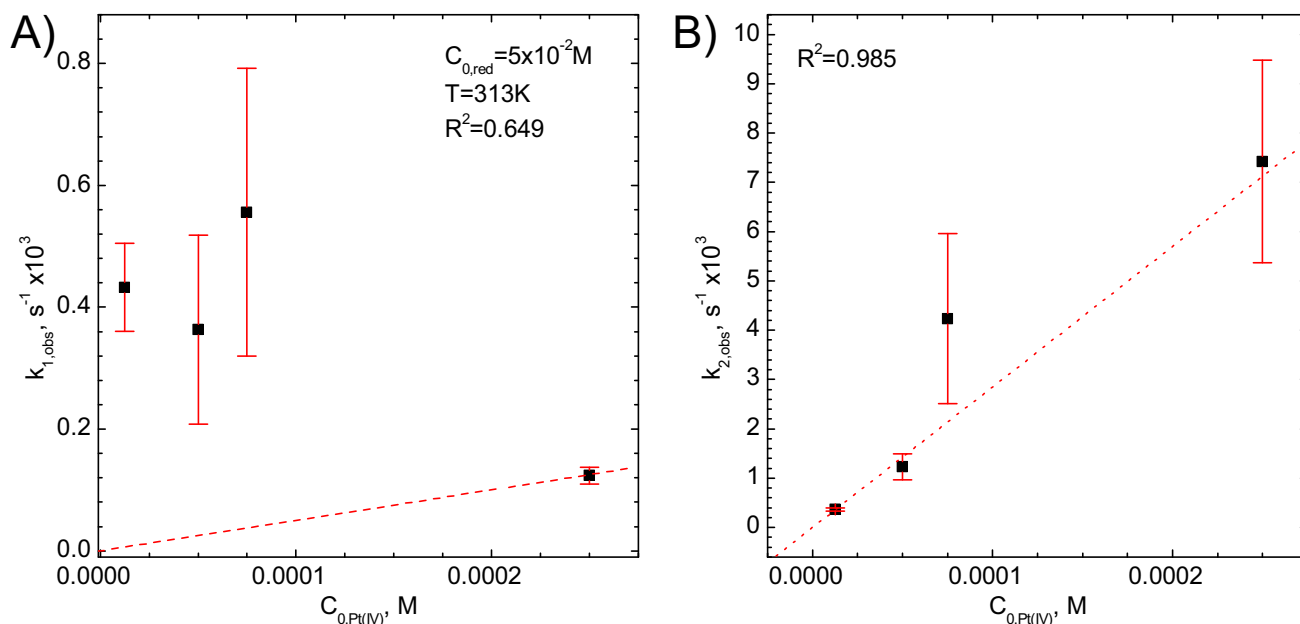


Fig. 3. The influence of the Pt(IV) chloride complex ions initial concentration on the observed rate constants

3.3. The influence of temperature on the reaction rate

The influence of temperature, between 308 and 328 K, on the observed rate constant was determined. This was further used for activation energy determination using Arrhenius equation:

$$k_{2,obs} = A \cdot e^{-\frac{E_a}{RT}} \quad (8)$$

where A stands for pre-exponential factor, E_a – activation energy, T – temperature, R – gas constant. The activation energy was determined only for $k_{2,obs}$ due to significant uncertainties of $k_{1,obs}$ determination.

From the practical point of view it is more comfortable to use the logarithmic form of eq. (8):

$$\ln k_{2,obs} = \ln A - \frac{E_a}{RT} \quad (9)$$

The activation parameters are gathered in Table 1.

TABLE 1

The Arrhenius equation's parameters

Intercept	Slope	E_a , kJ/mol	A , s ⁻¹
30.21 ± 1.36	-11254.36 ± 430.95	93.57	3.58 × 10 ¹³

It can be seen that the activation barrier is relatively high. The activation energy is equal to 93.57 kJ/mol. Therefore, the reduction process significantly depends on temperature.

3.4. The influence of ionic strength on the reaction rate

According to the Bronsted-Bjerrum theory, there is a significant impact of the ionic strength of the solution on the reaction

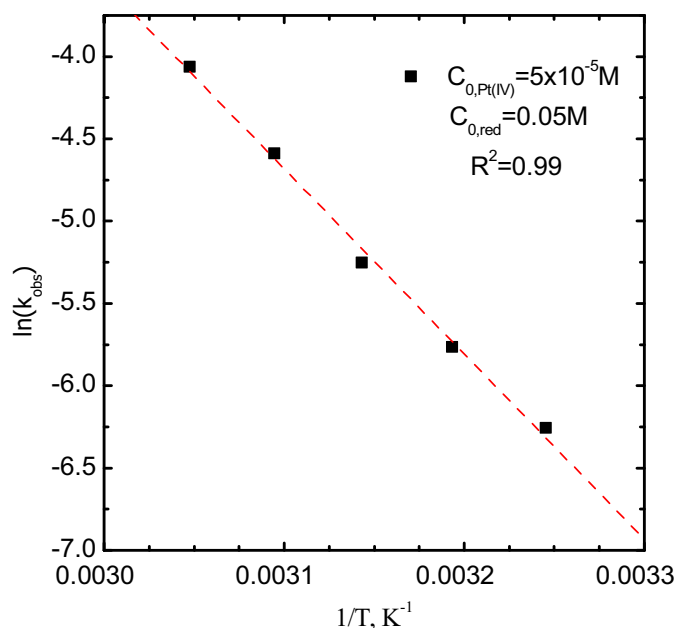


Fig. 4. Graphical determination of Arrhenius equation's parameters

rate. It is directly related to effect of stabilization of transition state. This effect is only visible, when reacting species are electrically charged. Thus, for reacting molecules it is negligible. The influence of ionic strength I on the observed rate constant is described with equation:

$$\log \left(\frac{k_{obs}}{k_{0,obs}} \right) = 2 \cdot a \cdot z_A \cdot z_B \cdot \frac{\sqrt{I}}{1 + \sqrt{I}} \quad (10)$$

where: $k_{0,obs}$ – the rate constant determined in the solution without NaClO₄ addition, $a = 0.509$ at 298 K for aqueous solutions, z_A and z_B are charges of the reacting species. The influence of

ionic strength of the solution on the observed rate constant of the second step of reduction was calculated for three hypothetical cases, where the reductant's charge was 0 and ± 1 and experimentally obtained $k_{2,obs}$ (Fig. 5).

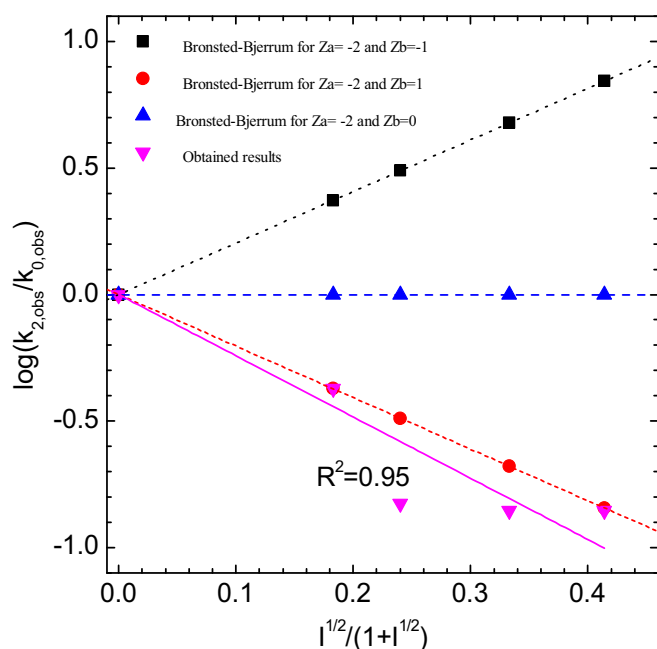


Fig. 5. Graphical determination of the reductant's charge

The charge of the reductant is equal to -1 . There is no doubt about that. However, results suggest that the platinum exhibit $2+$ charge. The deviation from the calculated line is caused by the uncertainties of observed rate constant determination. In such a case, it seems that the reaction is complex. Moreover, the obtained result suggests, that in the reaction PtCl_6^{2-} but other Pt(IV) structure. Therefore further studies are required.

3.5. The influence of chloride ions on the reaction rate

As it was shown above, the addition of an inert salt may affect the reaction kinetics. In this section, potassium chloride was added to the reaction mixture. The chloride ions are ligands for platinum complex ions and thus may affect the reduction kinetics. This again was studied only for $k_{2,obs}$ (Fig. 6).

As it can be observed, $k_{2,obs}$ decreases as the concentration of chloride ions increases. However, when the latter is above 0.005 M , it has no further effect on the observed rate constant. The influence of chloride ions on the observed rate constant in the studied range of Cl^- concentration can be described using the following empirical equation:

$$k_{2,obs}(\text{Cl}^-) = k_{2,0,obs} + B \cdot e^{R_0[\text{Cl}^-]} \quad (11)$$

where: $k_{2,0,obs}$ – the observed rate constant at the concentration of chloride ions going to infinity, equal to 0.00465 , B – fitted parameter equal to 0.00253 , R_0 – fitted parameter equal to -1010.05 .

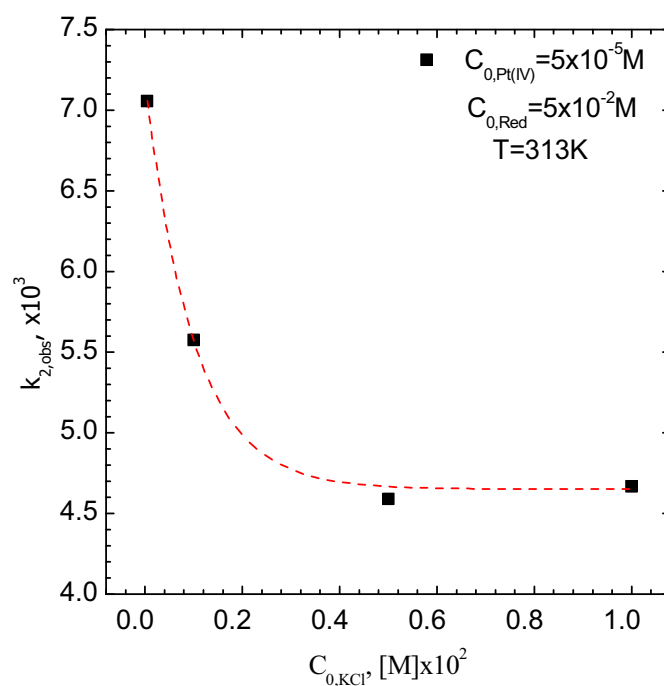
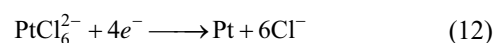


Fig. 6. The influence of chloride ions concentration on the observed rate constant

This empirical equation gives only scratch of the information about the reaction mechanism. To understand the phenomenon, more in-depth insight into the mechanism is required. The reaction between Pt(IV) and potassium formate, can be explained according to electrochemical theory. The theory assumes that two partial reactions in this case reduction of Pt(IV) and oxidation of formate ions, are not independent of each other and run simultaneously. The necessary condition for reactions and to occur is that the equilibrium potential for reductant oxidation is more cathodic than the corresponding potential for the metal ions reduction:



The equilibrium potential for Pt/PtCl_6^{2-} electrode defined by Nernst equation can be given as:

$$E_{0,\text{PtCl}_6^{2-}/\text{Pt}} = E_{\text{PtCl}_6^{2-}/\text{Pt}}^0 + \frac{RT}{4F} \ln \left(\frac{\text{PtCl}_6^{2-}}{(\text{Cl}^-)^6} \right) \quad (13)$$

In such a case, increase of chloride ions initial concentration, effects in decrease of the potential value. At constant equilibrium potential for formate ions (maintaining the isolation conditions), it results in a decreasing of the driving force of the reaction.

However, taking into account the results obtained using neutral salt and with potassium chloride, the following explanation can be taken. In the case of all presented results, the pH of the solution was equal to 4. The chloride concentration was close to 0, therefore it is probable that the Pt(IV) hydrolysis also occurs [18,19].

4. Conclusions

Taking into account obtained results, and observations, following conclusions can be drawn. First of all, the reaction rate is inhibited by chloride ions. This confirms, that the reaction of aqua complexes of Pt(IV) in the general form $\text{PtCl}_x(\text{H}_2\text{O})_y^{4-x+y}$ is faster than reaction of the preliminary assumed $\text{Pt}/\text{PtCl}_6^{2-}$ chloride complex. This observation is supported by the experiments related to the impact of chloride ions on the reaction rate. However, it cannot be excluded that the reaction involves other mixed complexes such as Pt(IV)-formate or Pt(IV)-Cl-OH⁻. DFT calculations indicated existence of In Pd(II)-formate complex [20].

High activation energy brings the explanation, why the process can be observed only at elevated temperature.

As it was confirmed, the reaction is autocatalytic, and finally leads to the formation of large particles at the bottom of the cuvette. This make this reaction suitable for the recycling of the platinum from highly diluted aqueous solutions. Losses associated with colloidal phase formation should be insignificant.

Acknowledgments

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