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THE MECHANISM OF REDOX REACTION BETWEEN PALLADIUM(II) COMPLEX IONS AND POTASSIUM FORMATE IN ACIDIC AQUEOUS SOLUTION

The kinetics studies of redox reaction between palladium(II) chloride complex ions and potassium formate in acidic aqueous solutions was investigated. It was shown, that the reduction reaction of Pd(II) is selective in respect to Pd(II) complex structure. The kinetic of the process was monitored spectrophotometrically. The influence of chloride ions concentration, Pd(II) initial concentration, reductant concentration, ionic strength as well as the temperature were investigated in respect to the process dynamics. Arrhenius equation parameters were determined and are equal to 65.8 kJ/mol, and A = 1.12×10^{11} s^{-1}.

Keywords: analysis; spectrophotometry; palladium; chloride; speciation, TD-DFT; recycling; recovery; kinetics; formate

1. Introduction

Palladium belongs to platinum group metal (PGM). It is one of the most important metals applied in catalysis, and there is one of the largest need for this metal. Also, palladium is often used in jewelry. However in this area, there is no grater problems with recycling.

The amount of palladium produced from primary sources is rather low. Most of the palladium is obtained as by-products. It is estimated that about 79% of world production of palladium is related to platinum mines in South Africa, and nickel mines in Russia.

Also an important source of palladium is an copper production industry where PGM as well as gold and silver often consist. One of the example is the Polish company KGHM, where silver, gold, palladium and platinum is obtained during the copper electrorefining. In this company, silver is separated in the first step. After that gold, platinum and palladium are leached at elevated temperature in concentrated hydrochloric acid, as an oxidant chlorine gas is used. Gold from the solution is precipitated in two steps using disodium disulphite ($Na_2S_2O_5$). After that mixture of trace of gold and significant amount of palladium and platinum remained in solution. Annual production of platinum and palladium in KGHM is equal to 93 kg (2008r) [1]. The amount strongly depend on the type of ores used in the process.

Finally, platinum and palladium are separated from the solution using sodium formate. As an final product mixture of those metals is obtained and in such a form is offered in the market.

Palladium can be recovered from aqueous system using several different methods, amount of them electrochemical [2-4], chemical [5], adsorption and/or ionic exchange [6,7].

The aim of this paper is to investigate and understand the process of palladium reduction reaction. Thanks to that knowledge might to be possible to selective separate palladium and platinum using sodium or potassium formate due to difference in the reaction kinetics. To make it possible the knowledge of kinetics of the reduction reaction of each metal consisting in the system is required.

2. Experimental

The Pd(II) precursor was obtained by dissolution of 10 g of $PdCl_2$ salt in stoichiometric amount of concentrate hydrochloric acid (37%, Avantor Performance Materials, A.R.). Then, obtained solution was complemented to 0.5 dm^3, using 0.1 M hydrochloric acid. In such a way obtained stock solution, was later dissolved, to obtain required concentration.

As an reductant potassium formate was applied (HCOOK, A.R. 99%>). In all experiment deionized water was applied (Hydrolab HLP-30, Na$^+$, SO$_4^{2-}$, Cl$^-$, Br$^-$, NO$_2^-$, NO$_3^-$, PO$_4^{3-}$ < 0.5 ppb, Fe, Zn, Cu, Cr, Mn < 0.1 ppb, conductivity < 0,07 S/cm).

As it is well known, the palladium (II) chloride complex ions are colored. Thanks to that it is possible to monitor their concentration in the solution using spectrophotometric method.

The UV-Vis spectra were registered using spectrophotometer Shimadzu model U-2501PC. Moreover, the stopped-flow technics was applied for the reaction kinetics investigation. For this purpose the Applied Photophysic, model XS-20 was used.

It is well known, that the palladium(II) chloride complex in effect of pH and/or chloride ions concentration changes, may

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change the structure. There is a several papers where $Pd^{2+}-Cl^--H_2O-OH^-$ system was described [8-13].

The simulations of Pd(II) complexes structure were done using TD-DFT method according to our previous work [14]. Theoretical modeling was performed with Gaussian 09 Rev. D.01 (Gaussian, Inc.) The final geometry was obtained by using DFT with the B3LYP (the Becke three-parameter-Lee-Yang-Parr) functional and the LanL2DZ basis set. Molecular orbitals and surfaces were plotted using GausView 5 software. Electronic transitions were calculated by using time-dependent TD-DFT with the B3LYP functional and the LanL2DZ basis set. In addition the electronic spectra were calculated assuming water as a solvent using the IEFPCM method [15]. UV-Vis spectra were analyzed using Origin 8.5 software.

In general, palladium(II) aqua complex formation in chloride ions containing media can be described by several reaction steps. Those reactions as well as related to them, stability constants are gathered in Table 1.

Taking into account, given above stability constants, the share of Pd(II) form can be calculated. It is well known that, at low values of pH, aqua complexes might dominate, where in alkaline environment hydroxyl complexes plays an important role. Therefore in, Table 2 only aqueous complexes were taken into account.

As it can be seen, there is significant impact of chloride ions concentration on the form of Pd(II) complexes existing in the solution.

All experiments were repeated five times. Given error bars corresponds to standard deviation.

TABLE 1

The reaction scheme as well as related to them, stability constants

Reaction scheme	Stability constant ($\log(K_x)$)	Ref.	Eq.
$[PdCl_4]^{2-} + H_2O \xrightleftharpoons{K_1} [PdCl_3(H_2O)]^- + Cl^-$	5.08	[8]	(1)
$[PdCl_3(H_2O)]^- + H_2O \xrightleftharpoons{K_2} [PdCl_2(H_2O)_2]_{cis} + Cl^-$	3.475	[8]	(2)
$[PdCl_3(H_2O)]^- + H_2O \xrightleftharpoons{K_3} [PdCl_2(H_2O)_2]_{cis/trans} + Cl^-$	2.1	[8]	(3)
$[PdCl_2(H_2O)_2]_{cis/trans} + H_2O \xrightleftharpoons{K_4} [PdCl(H_2O)_3]^+ + Cl^-$	0.902	[8]	(4)
$PdCl_4^{2-} + OH^- \xleftarrow{K_5} PdCl_3OH^{2-} + Cl^-$	4.81	[16]	(5)
$PdCl_3OH^{2-} + OH^- \xleftarrow{K_6} PdCl_2(OH)_2^{2-} + Cl^-$	4.15	[16]	(6)
$PdCl_2(OH)_2^{2-} + OH^- \xleftarrow{K_7} PdCl(OH)_3^{2-} + Cl^-$	3.39	[16]	(7)
$PdCl(OH)_3^{2-} + OH^- \xleftarrow{K_8} Pd(OH)_4^{2-} + Cl^-$	2.21	[16]	(8)

TABLE 2

Fraction of Pd(II) aqueous complexes in the solution containing different concentration of chloride ions

Pd(II) complex fraction, %	[Cl⁻], M				
	1	1×10^{-1}	1×10^{-2}	1×10^{-3}	1×10^{-4}
$[PdCl_4]^{2-}$	27.81	1.72	0.02	0.00	0.00
$[PdCl_3(H_2O)]^-$	63.10	39.03	4.15	0.09	0.00
$[PdCl_2(H_2O)_2]_{cis/trans}$	9.03	55.87	59.42	12.58	0.66
$[PdCl(H_2O)_3]^+$	0.05	3.37	35.87	75.95	39.75
$[Pd(H_2O)_4]^{2+}$	0.00	0.01	0.54	11.38	59.59

3. Results

It was found that at low pH, the reaction did not accrue, until the pH of the solution was below 3. In Fig. 1A an example of UV-VIS spectrum of palladium(II) complexes at low pH is shown. As it can be seen there are three peaks observed. After the changes of pH from 1 to 4 (see Fig. 1B) significant changes in

UV-VIS spectrum can be observed. This might to be related with changes of Pd(II) complexes share. In Fig. 1C molar absorption coefficient was determined using graphical method. As it can be seen, there is linear correlation between concentration of Pd(II) and absorbance level. In Fig. 1D an example of kinetic curve of Pd(II) reduction by potassium formate is shown.
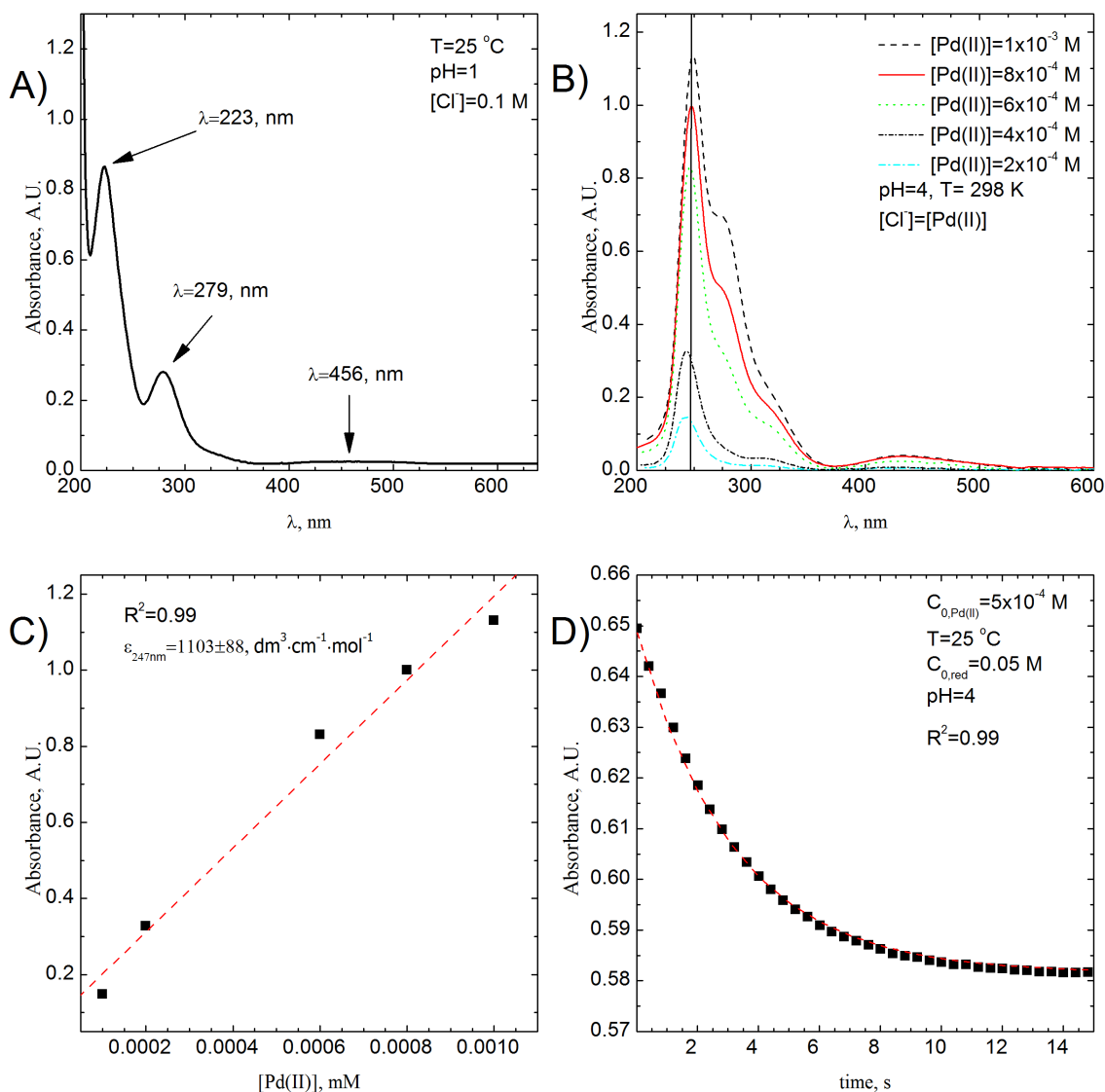
Fig. 1. A) UV-VIS spectrum of Pd(II) chloride complexes at pH = 1 and [Cl⁻] = 0.1M, B) UV-VIS spectra's of Pd(II) complexes at pH = 4 and [Cl⁻] = [Pd(II)], C) graphical determination of molar absorption coefficient, D) kinetic curve of Pd(II) complexes reduction using potassium formate experimental conditions: pH = 4, T = 25°C, [Pd(II)] = 5×10⁻⁴M, [$C_{0,red}$] = 0.05 M

As it can be seen, kinetic curve has exponential shape, and can be described by following equation:

$$C_{Pd(II),t} = C_{Pd(II),0} \cdot e^{-k_{obs} \cdot t} \qquad (9)$$

Also it has to be noted, that the reaction is fast. After c.a. 14 seconds, plato is observed. This suggest, that either there is stereo selectivity, where only one form of Pd(II) is reduced, or Pd(II) formate complexes might to be formed in the system, similar to silver-formate salt [17].

3.1. The influence of Pd(II) initial concentration

Assuming pseudo first order reaction, the influence of Pd(II) initial concentration on observed rate constant was investigated using stopped flow method.

As it can be seen, the increase of Pd(II) initial concentration effects in decrease of observed rate constant. Observed depend-
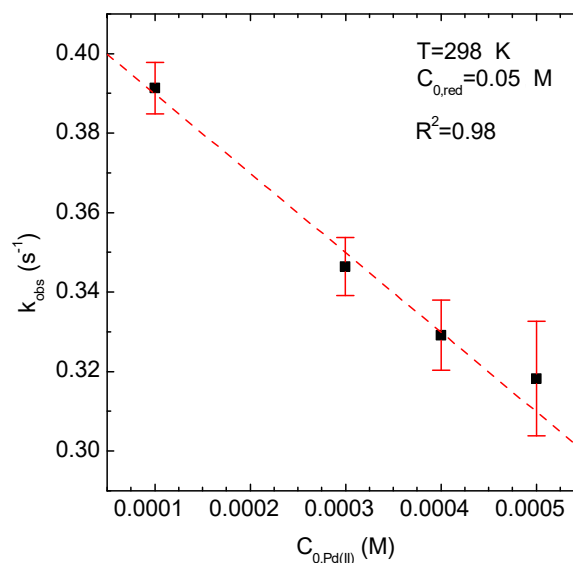

Fig. 2. The influence of Pd(II) initial concentration on the observed rate constant

ence is linear in the investigated range of Pd(II) concentration. It has to be noted that in each case, excess of reductant was kept. This suggest that studied process is complex. To understand this phenomenon, further analysis are required.

3.2. The influence of temperature on the reaction rate

The influence of temperature on the k_{obs} can be described by the Arrhenius equation:

$$k_{obs} = A \cdot e^{\left(-\frac{E_a}{R \cdot T}\right)} \tag{10}$$

where: A – pre exponential factor, E_a – activation energy, T – temperature, R – gas constant.

The activation energy can be determined using logarithmic form of (Eq. 10):

$$\ln(k_{obs}) = \ln(A) - \frac{E_a}{R \cdot T} \tag{11}$$

The slope and intercept of $\ln(k_{obs})$ vs. $1/T$ dependence corresponds to E_a and A, respectively. Obtained results are shown in Fig. 3.

Values of activation energy as well as the pre exponential factors are gathered in Table 3.

Fig. 3. The influence of temperature on the observed reaction rate. Experimental conditions: [Pd(II)] = 5×10⁻⁴M or 4×10⁻⁴M, [C_red] = 0.05M, pH = 4

It was found that activation energy is independent in respect to initial concertation of Pd(II) complexes and is equal to 66kJ/mol.

3.3. DFT simulation

To understand the mechanism of the reaction, several different simulation using density functional theory (DFT) were performed. In Fig. 4A, registered UV-VIS spectrum of the solution containing Pd(II) complexes before mixing with potassium formate. In Fig. 4B calculated UV-Vis spectrum using time dependent density functional theory (TD-DFT) is shown. As it

TABLE 3

Parameters of Arrhenius equation

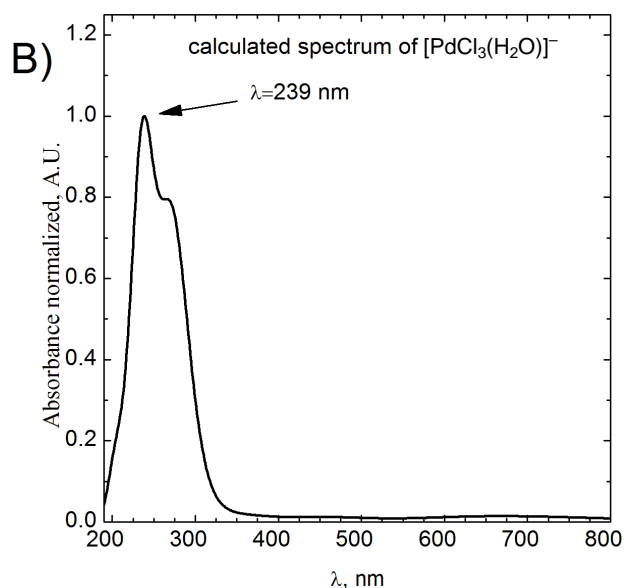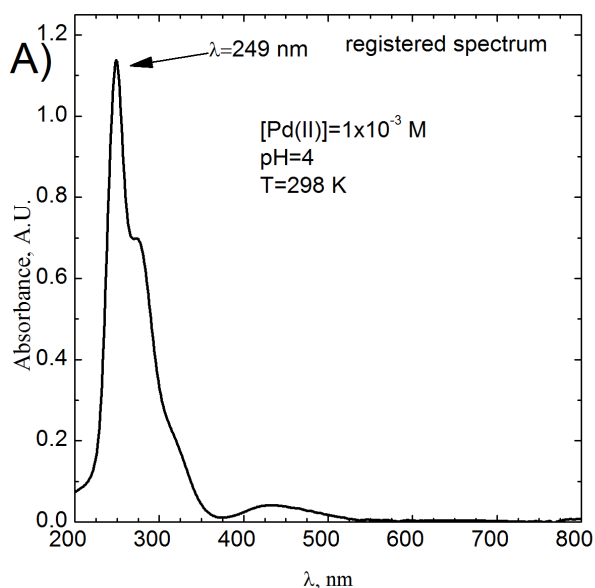| Reagents concentrations	$-\dfrac{E_a}{R}$	$\ln(A)$	E_a, kJ/mol	A, s⁻¹
[Pd(II)] = 5×10⁻⁴ M, [C_{0,red}] = 0.05 M	−7910.61	25.44	65.77	1.12·10¹¹
[Pd(II)] = 4×10⁻⁴ M, [C_{0,red}] = 0.05 M	−7976.81	25.62	66.32	1.34·10¹¹

Fig. 4. A) registered UV-VIS spectrum of the solution containing Pd(II) complexes, B) calculated using DT-DFT method UV-VIS spectrum of [PdCl₃(H₂O)]⁻ complex

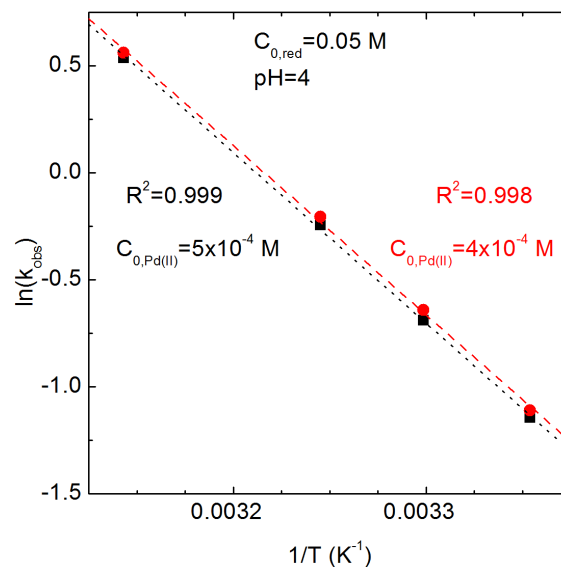can be seen there is an excellent agreement between registered and calculated spectrum.

Slight red shift of the peak can be explained by superposition of other peaks coming from other forms of Pd(II) complexes existing in the system at the equilibrium state (mainly [PdCl$_2$(H$_2$O)]$_{cis}$) [14].

After mixing of Pd(II) complex with potassium formate, fast decrease of absorbance at the wavelength 249 nm is observed. After c.a. 1 min, UV-Vis spectrum was registered and is shown in Fig. 5.

As it can be seen, there is no sharp peaks in the spectrum. This clearly confirm, that the structure of Pd(II) complex is changed, and probably several form exists in the system.

Preliminary we assume two possible forms of Pd(II) – formate complexes which are shown in Fig. 6. First of them is structure where palladium is connected with two molecules of formate (Fig. 6A) and the second one is palladium connected with one molecule of formate and two atoms of chloride (Fig. 6B). For this complex the optimization of the structures were done. Calculated total energy for PdMr$_2$ complex is lower (−504,982) than for PdMrCl$_2$ complex (−345,982). These value confirm that PdMr$_2$ complex is more stable structure and probability of its existence in the system is high. Using TD-DFT method, the UV-VIS spectra were calculated for both complexes (Fig. 6A and B).

Obtained results confirm previous assumption, because comparison experimental (Fig. 5) and calculated (Fig. 6A) spectra for PdMr$_2$ complex we can see good agreement in peak position. (however the intensity of peak is different, because theoretical model don't take into account all interactions in solution). In registered spectrum the most intensive peak about 214 nm (216 nm in calculated spectrum) is related to electron transfer from HOMO-2 to LUMO+1. Another peak about
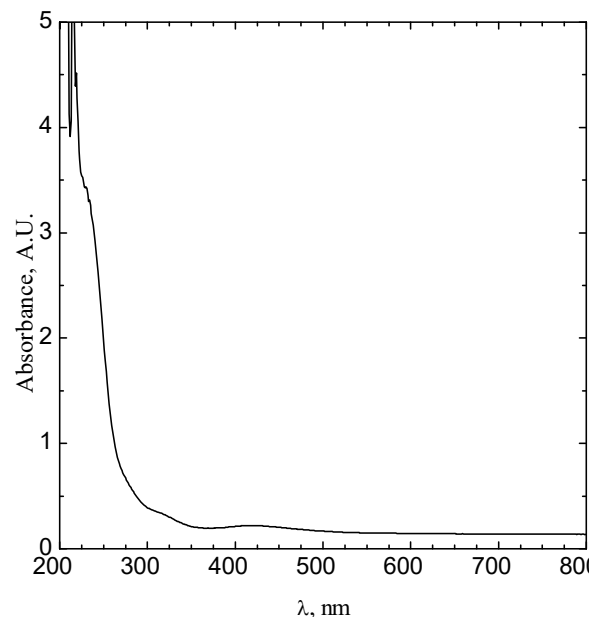

Fig. 5. UV-VIS spectrum of the solution after c.a. 1 min after reagent mixing

230 nm (238 nm in calculated spectrum) is caused by electron transfer from HOMO-1 to LUMO. The next two peaks: ~250 and ~320 nm (273 and 333 nm in calculated spectrum) are related to electron transfer from HOMO-3 and HOMO-5 to LUMO. (Some devotion, probably related to presence of Pd-Cl-H$_2$O complexes in the solution).

In Fig. 7 HOMO and LUMO state for PdMr$_2$ is shown.

As it can be seen, at the HOMO state, the charge density is mainly located on Palladium atom, where in case of LUMO the charge is transferred mainly on the ligand sites.
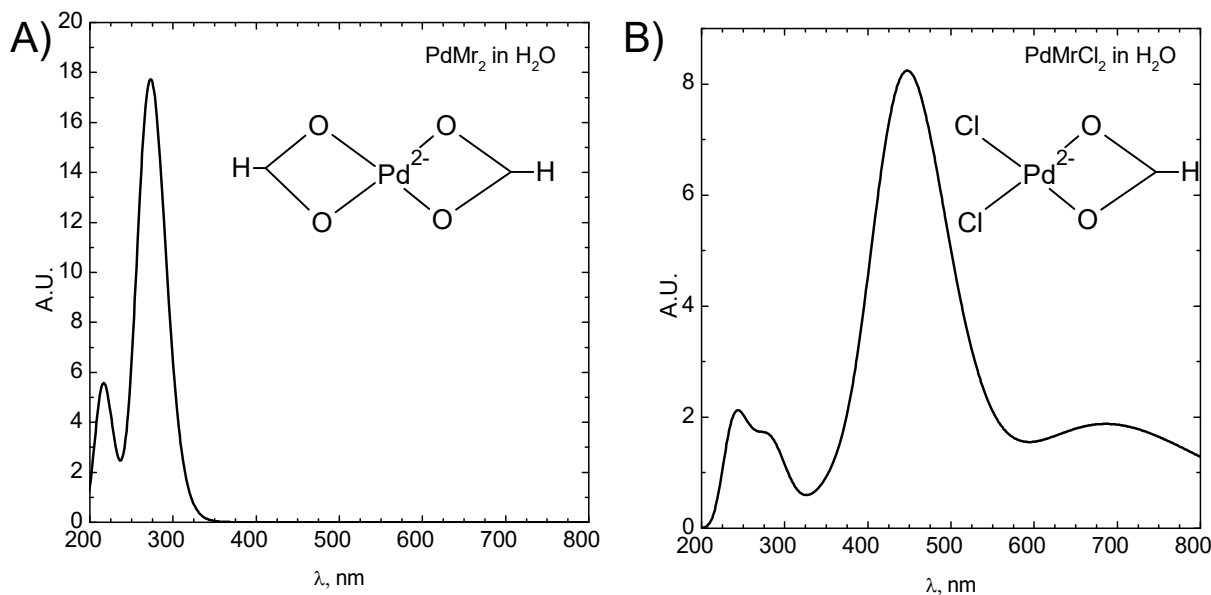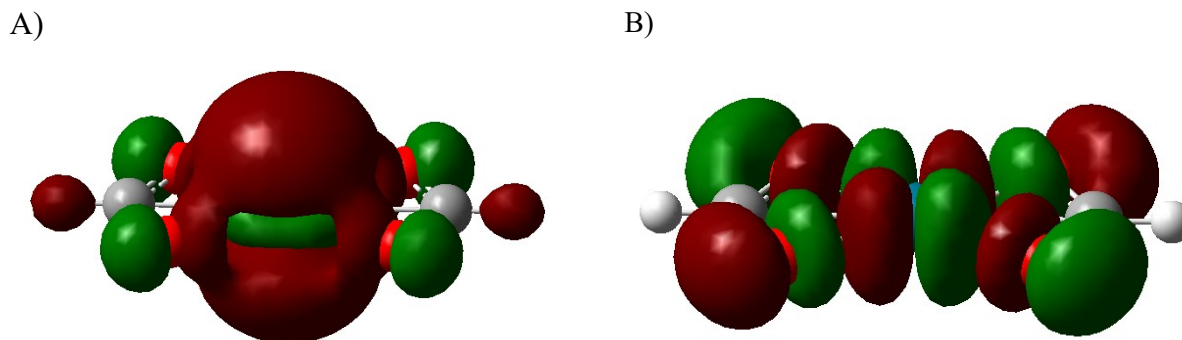

Fig. 6. TD-DFT simulation of UV-VIS spectrum of proposed Pd(II) formate complexes

Fig. 7. Orbital structure of $PdMr_2$ A) HOMO, B) LUMO

3.4. The influence of reductant initial concentration on the reduction process

On the basis of the decay of the absorption spectrum of the Pd(II) species, at the characteristic wavelength, ie. 242 nm kinetic curves were prepared (measurements were performed using Shimadzu spectrophotometer). Then, on the basis of the so determined kinetic curves for different concentrations of the reductant observed rate constants were determined. In addition, the turbidance was observed. It was assumed that the increase of turbidance is directly related to the metallic palladium formation in the solution in the form of colloidal suspension.

In Fig. 8 an examples of kinetic curve of Pd(II) complexes reduction by potassium formate is shown. As it can be seen,
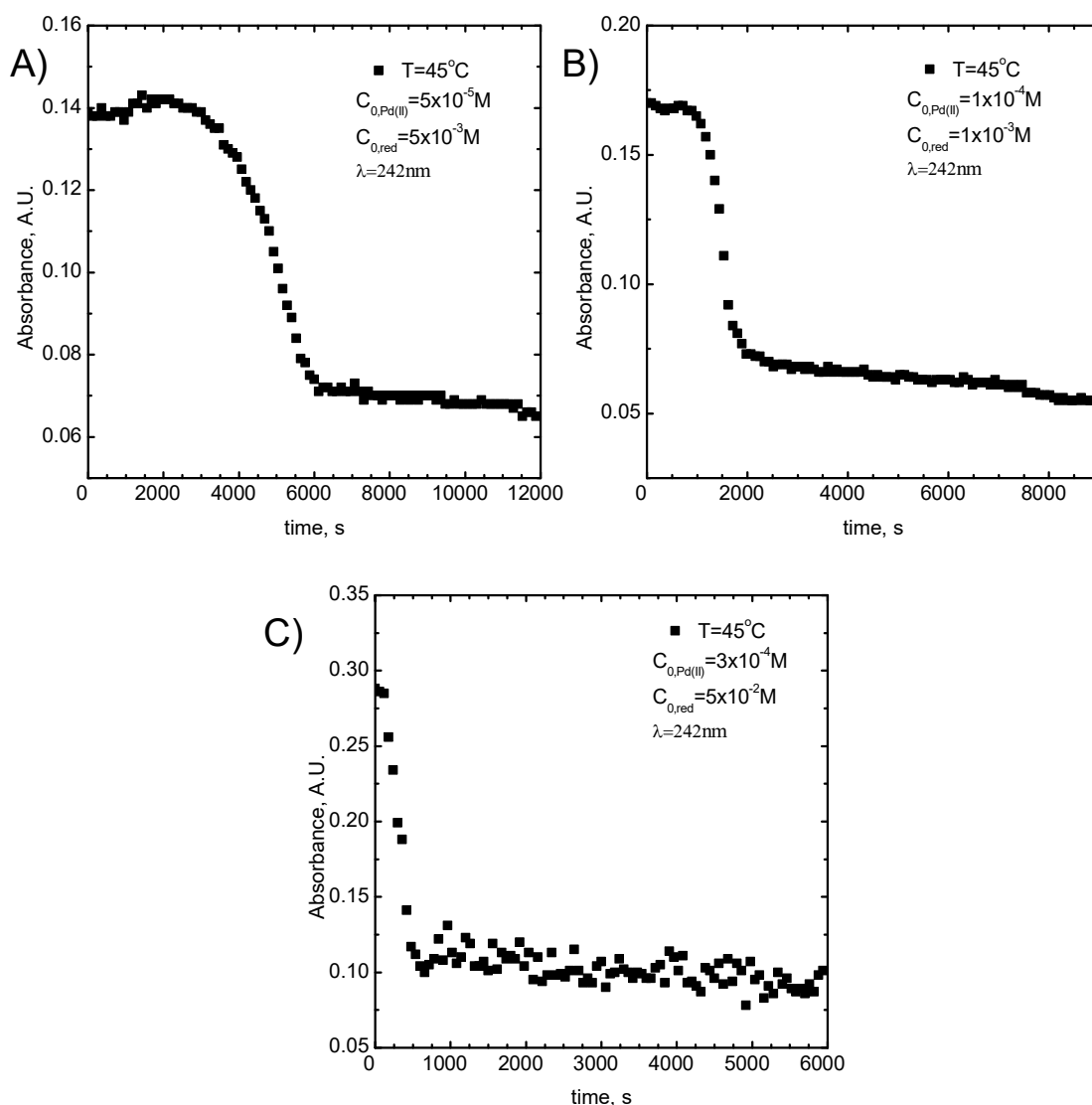

Fig. 8. An examples of kinetic curve of the reduction reaction

the kinetic curves have specific sigmoidal shape. This in turn suggest that the next step of the reaction is autocatalytic. It has to be underlined, that it this case time scale is significantly different then in experiment described above. Therefore, different spectrophotometer was applied.

Again, it can be seen, that the value of absorbance after some period time is reaches constant value different from zero. In this case it is related to the overlapping of two optical effects, the first one is related to the light absorption by Pd(II) complexes and the second one is related to the light scattering by metallic palladium particles.

To determine the rate constants describing the disappearance of Pd(II) complexes model Finke-Watzky [18] was used. This model assumes the existence of two parallel chemical processes of which the second is a catalytic process, the first reaction catalysed products. Schematically, this can be written as follows:
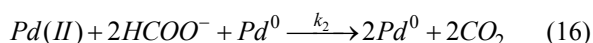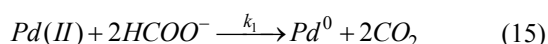
$$A \xrightarrow{\;k_1\;} B \qquad (12)$$

$$A + B \xrightarrow{\;k_2\;} 2B \qquad (13)$$

Decay of component A (in this case Pd(II) complexes) can be described as follow:

$$[A] = \frac{[A]_0 + \dfrac{k_1}{k_2}}{1 + \dfrac{k_1}{k_2[A]_0} \cdot e^{(k_1 + k_2[A]_0)\cdot t}} \qquad (14)$$

Index „0" denote initial concentration.

We suggest, that the reaction mechanism might to be described by following equations:

$$Pd(II) + 2HCOO^- \xrightarrow{\;k_1\;} Pd^0 + 2CO_2 \qquad (15)$$

$$Pd(II) + 2HCOO^- + Pd^0 \xrightarrow{\;k_2\;} 2Pd^0 + 2CO_2 \qquad (16)$$

Taking in to account that the experiments were carried out with the application of significant excess of reductant, the changes of it concentration can be neglected. Under this assumption, equations given above, can be rearranged and given in the following form:

$$Pd(II) \xrightarrow{\;k_{1,obs}\;} Pd^0 \qquad (17)$$

and

$$Pd(II) + Pd^0 \xrightarrow{\;k_{2,obs}\;} 2Pd^0 \qquad (18)$$
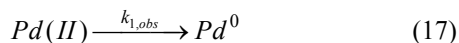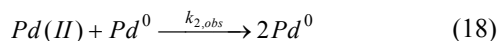
where:

$$k_{1,obs} = k_1 \cdot 2[HCOO^-] \qquad (19)$$

and

$$k_{2,obs} = k_2 \cdot 2[HCOO^-] \qquad (20)$$

Under such an assumption, the decrease of palladium concentration can be described by following equation:

$$[Pd(II)] = \frac{[Pd(II)]_0 + \dfrac{k_{1,obs}}{k_{2,obs}}}{1 + \dfrac{k_{1,obs}}{k_{2,obs}[Pd(II)]_0} \cdot \exp(\dfrac{k_{1,obs}}{k_{2,obs}} + [Pd(II)]_0)k_{2,obs}t} \qquad (21)$$

Equation given above, was used to determine the rate of Pd(II) complexes reduction to the metallic form.
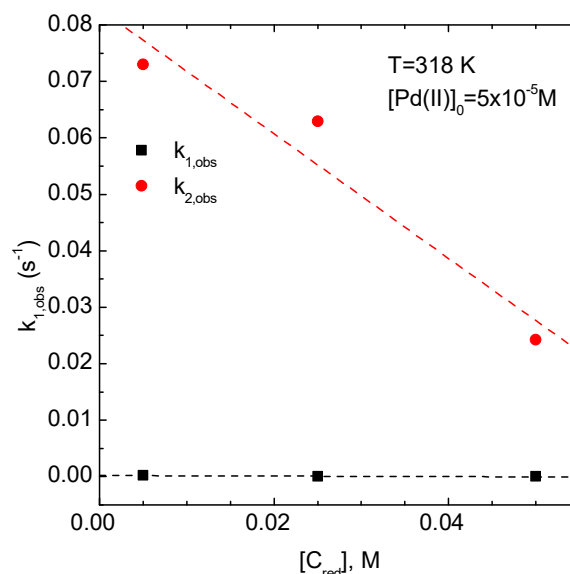

Fig. 9. The influence of reductant initial concentration on the observed rate constant

The value of the observed rate constant $k_{1,obs}$ increases with increasing initial concentration of the reductant, which is consistent with the assumed model. In case of observed rate constant of $k_{2,obs}$ it decreases with the increase of initial concentration, which is inconsistent with the assumed model.

It is postulated that in the studied process heterogeneous (catalytic) reaction is dominant and determines the overall reaction rate, while the homogeneous reaction reaction is slow. In this case, the acceleration of the formation of the catalyst should result in a sharp acceleration of reaction in a heterogeneous system. It is not excluded that the increase in the initial concentration of potassium formate in solution shifts the equilibrium adsorption of the salt on the surface of the catalyst. This in turn, effects in decreasing of the observed reaction rate $k_{2,obs}$.

3.5. The influence of ionic strength

The influence of ionic strength on the reaction rate was also investigated. For this purpose lithium perchlorate was used (LiClO_4, Avantor, A.P). Obtained results are shown in Fig. 10A and B.

As it can be seen, increase of ionic strength effects in increase of observed rate constants $k_{1,obs}$ and $k_{2,obs}$. Especially in case of $k_{2,obs}$ this effect is strong. It has to be recalled, that $k_{2,obs}$ is related to the heterogeneous reaction. It is well known, that metallic nanoparticles have strong negative surface charge, which depends on the concentration of salt. This might to explain the positive effect of salt concentration on the observed rate constant $k_{2,obs}$.
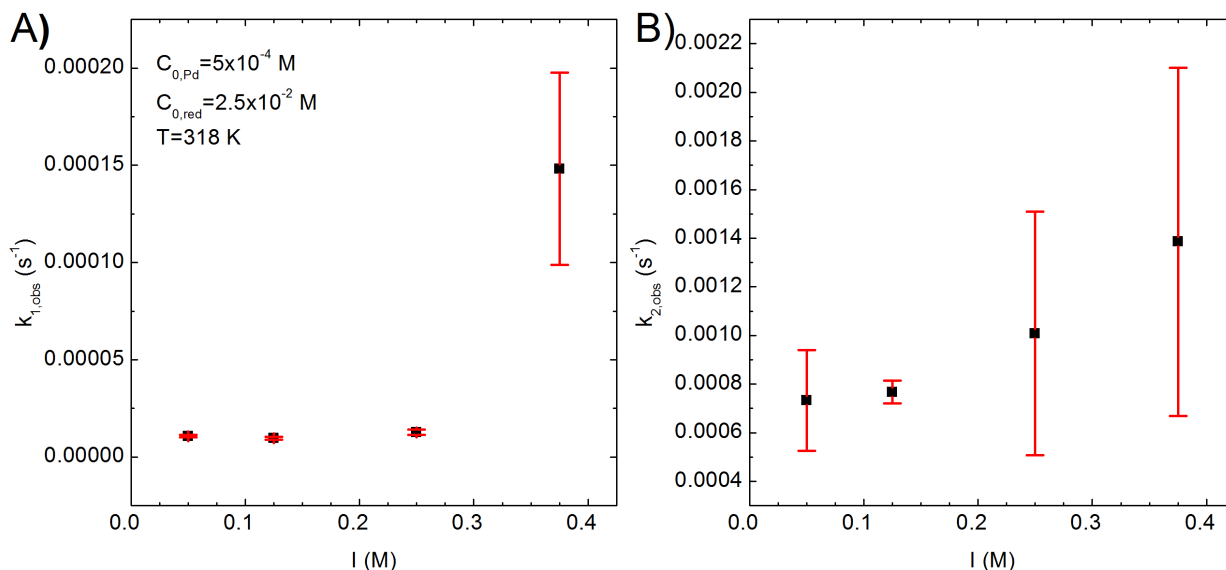
Fig. 10. The influence of ionic strength on the observed rate constants

3.6. The influence of chloride ions concentration

The influence of chloride ions concentration on the observed rate constant was investigated. For this purpose potassium chloride was applied. Obtained results are shown in Fig. 11.

As it can be seen, there is no influence of chloride ions concentration on observed rate constant $k_{1,obs}$, while there is strong impact on the observed rate constant $k_{2,obs}$. This effect can be described by following equation:

$$k_{2,obs}(Cl^-) = 2.85 \cdot 10^{-5} + 4.82 \cdot 10^{-4} \cdot e^{80 \cdot [Cl^-]} \quad (22)$$

This effect is clearly related to the form of Pd(II) complexes, increase of Cl^- concentration shift the equilibrium. In effect, chloride complexes of Pd(II) dominating in the system, where for low concentration of Cl^- aqueous complexes are more preferred (see Table 2)

3.7. Solid phase precipitation

In Fig. 12A and B, an example of reduction kinetic curve as well as solid phase precipitation are shown respective.

Maximum of turbidance is observed after c.a. 10000s, after that slow decrease of turbidance is observed. This is related to the formation of larger aggregates and it's sedimentation. On the bottom of quartz cuvette after experiment black powder was observed.

4. Conclusions

Studied process consist of several steps. The first one is probably related to the palladium – formate complex formation. This process is quiet fast, and those complexes are rather stable.
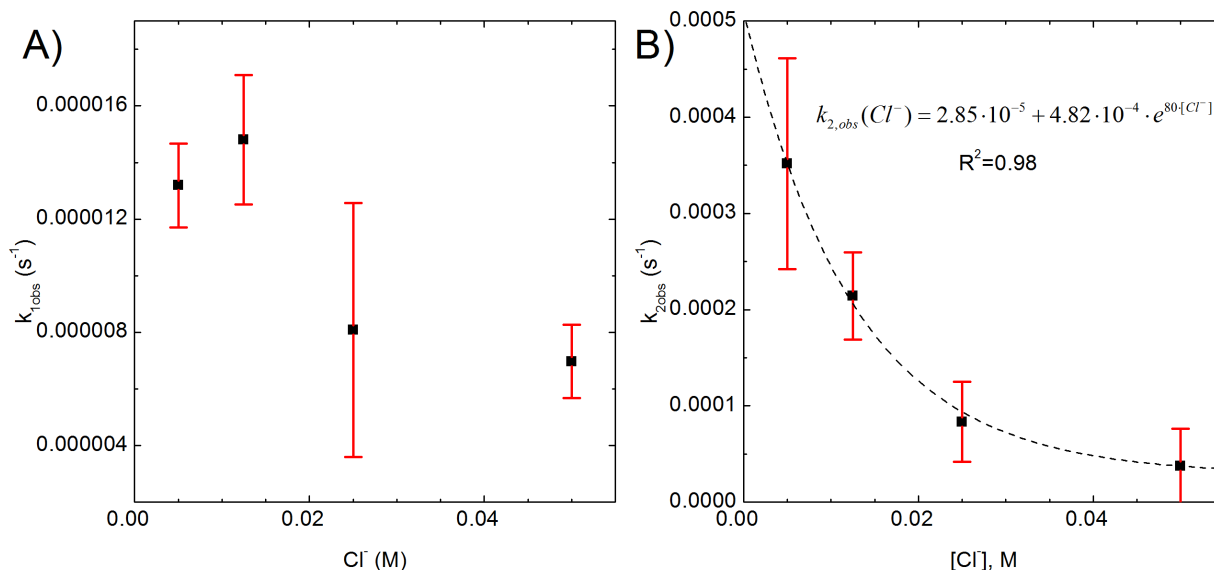

Fig. 11. The influence of chloride ions concentration on the observed rate constant
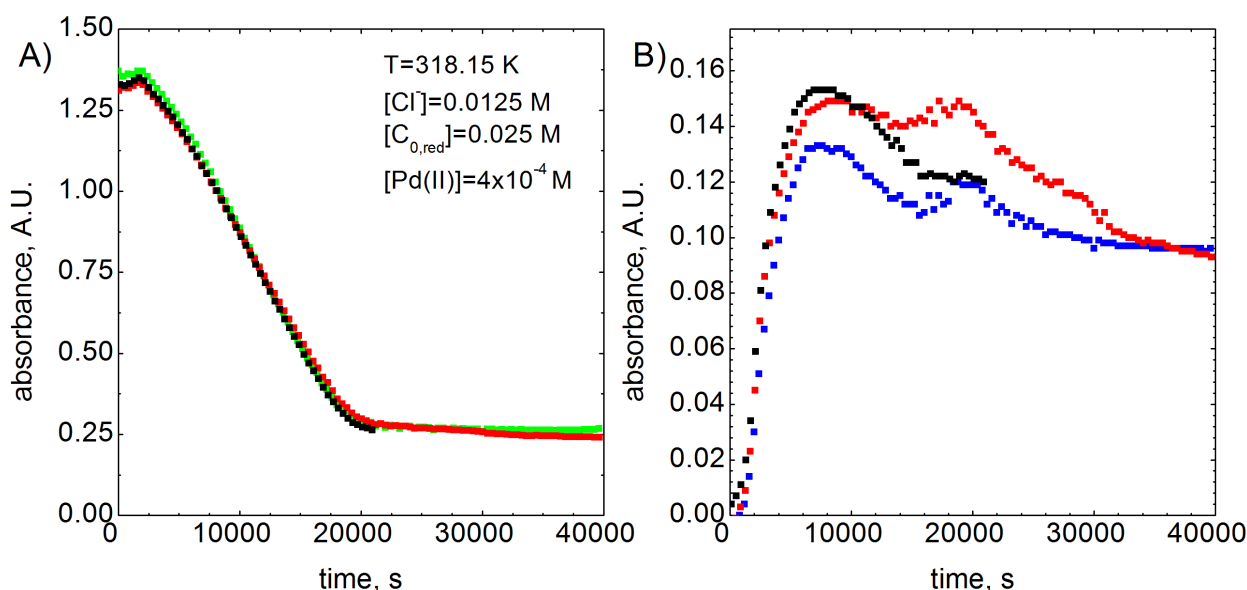
Fig. 12. A) decrease of Pd(II) concentration v.s. time, and B) solid phase formation v.s. time. Experimental conditions: $T = 318.15$ K, Cl$^-$ = 0.0125 M, $C_{0,red}$ = 0.025 M, $C_{0,Pd(II)}$ = 4×10^{-4} M

Significant excess of potassium formate is required to obtain solid metallic precipitate.

Reduction of palladium-formate complex is autocatalytic. Metallic palladium significantly accelerate the rate of the Pd(II) reduction. This in turn effect in large particles formation what is desirable in hydrometallurgy. Thanks to that metallic phase can be easily separated, and metal losses significantly decreased.

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