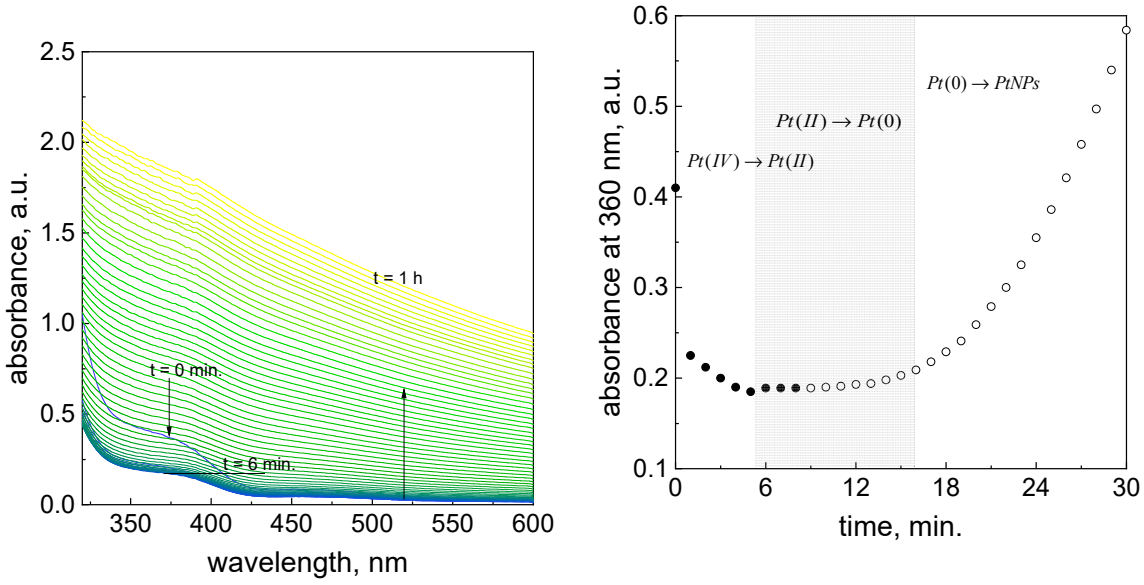
## Supplementary Materials

# The Kinetics of the Redox Reaction of Platinum(IV) Ions with Ascorbic Acid in the Presence of Oxygen

**Magdalena Luty-Błocho [1,*], Aleksandra Szot [1], Volker Hessel [2] and Krzysztof Fitzner [1]**

[1] Faculty of Non-Ferrous Metals, AGH University of Krakow, al. Adama Mickiewicza 30, 30-059 Kraków, Poland; szot@agh.edu.pl (A.S.); fitzner@agh.edu.pl (K.F.)
[2] School of Chemical Engineering, The University of Adelaide, Adelaide 5005, Australia; volker.hessel@adelaide.edu.au
* Correspondence: mlb@agh.edu.pl; Tel.: +48-12-617-4126

S1. The spectra evolution in the course of the PtNPs formation.




(**a**) (**b**)

**Figure S1.** The change in the turbidity level characteristic for the process of platinum nanoparticles formation (a), kinetic curve registered at 360 nm (b). Conditions: $C_{0,\,Pt(IV)}$ = 1.0 mM, $C_{0,\,H2Asc}$ = 60 mM, pH = 2.50 ± 0.05, T = 313 ± 0.1 K, I = 0.06 M.

S2. The Arrhenius and Eyring dependency

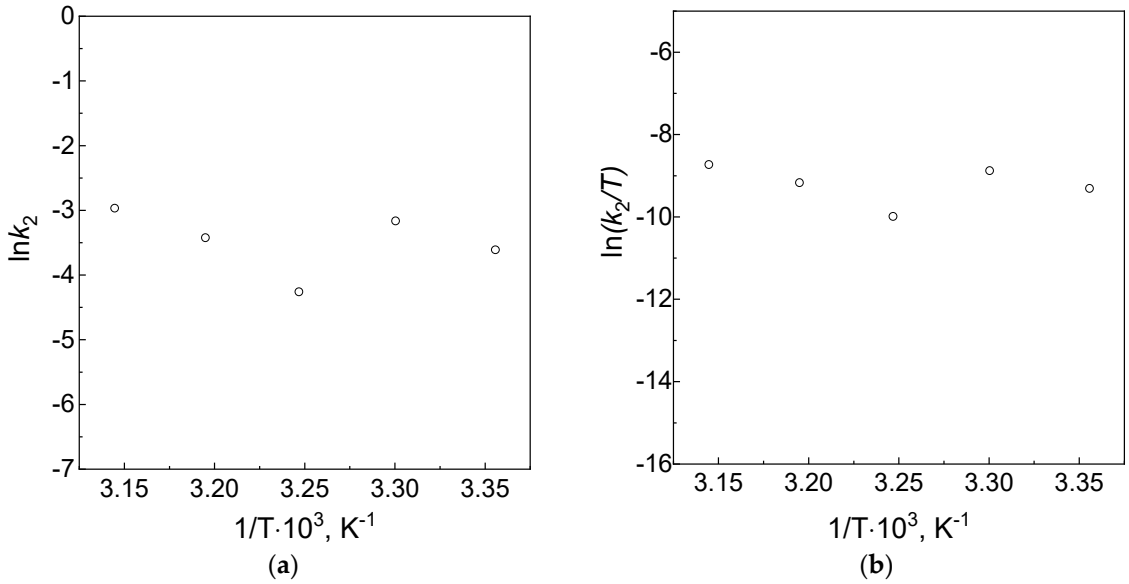
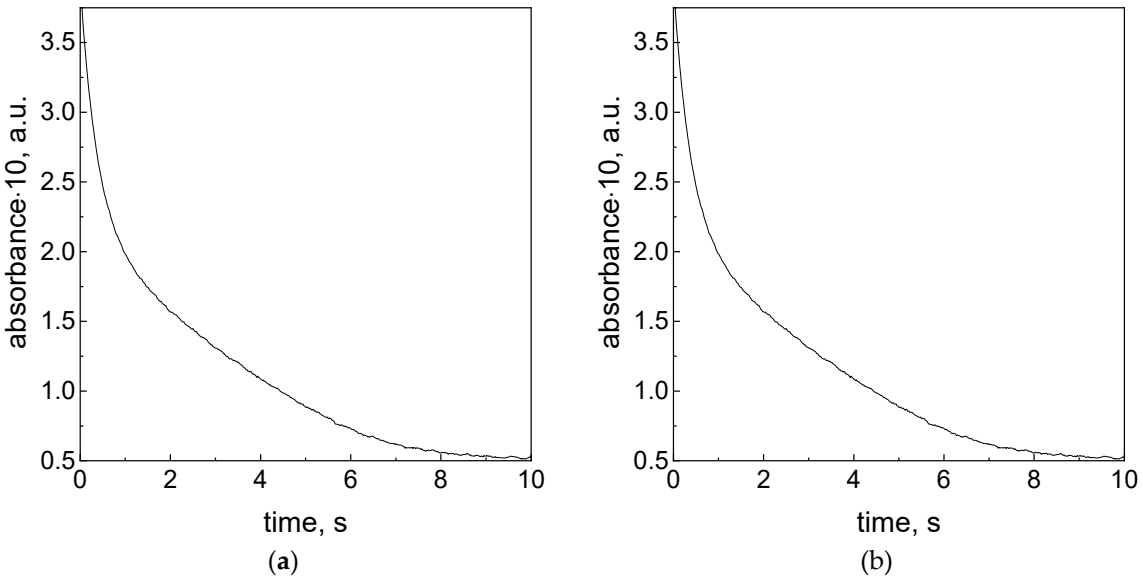



**Figure S2.** Arrhenius (a) and Eyring (b) dependency for reduction of Pt(IV) ions using ascorbic acid. Conditions: $C_{0,Pt(IV)}$ = 1.0 mM, $C_{0,H2Asc}$ = 60 mM, pH = 2.50 ± 0.05, I = 0.06 M.

S3. The kinetic curves registered at different pH of the solution.



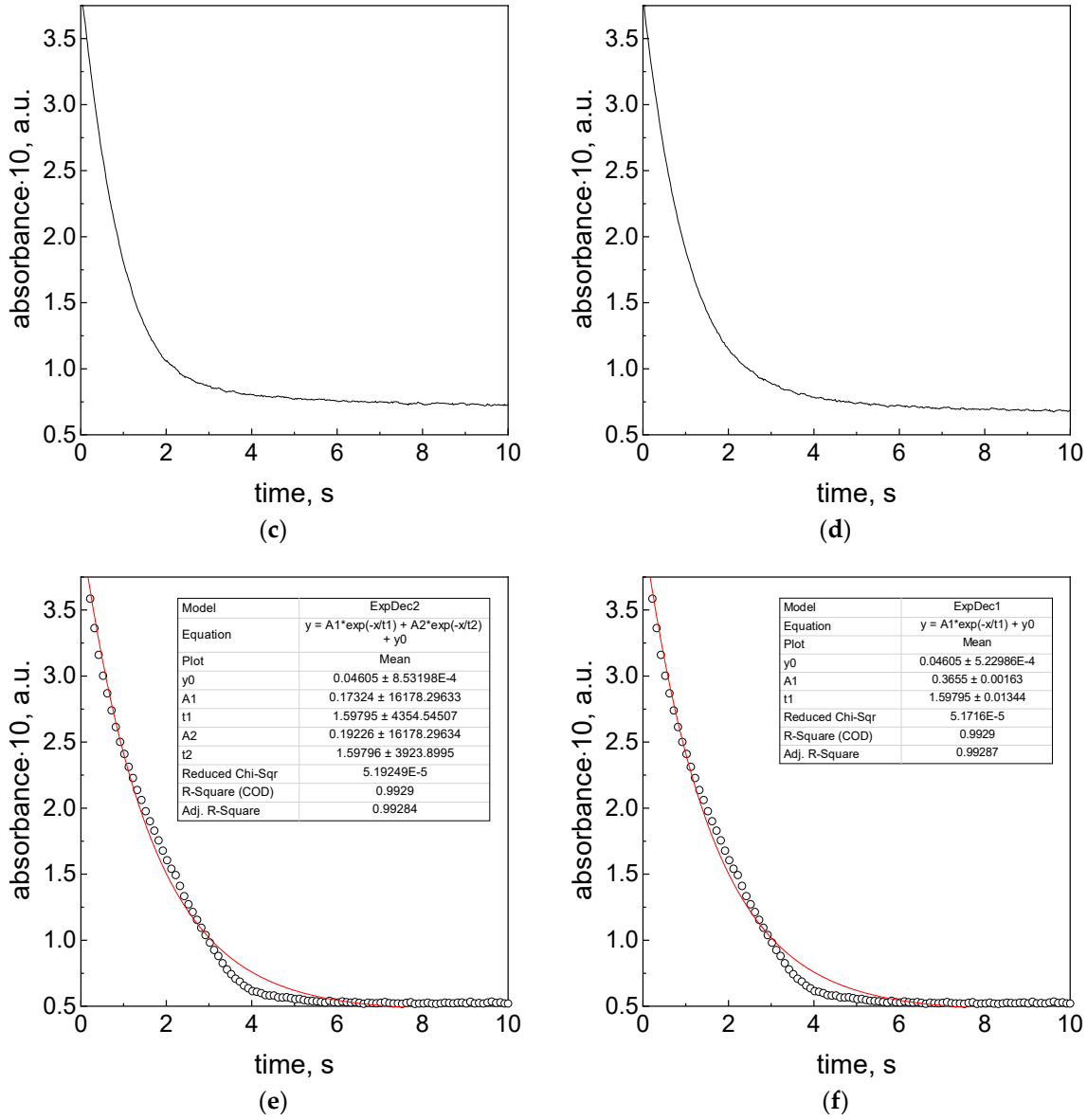



**Figure S3.** The sample of kinetic curves at different pH levels of the solution, registered during Pt(IV) ion reduction using ascorbic acid: pH = 2.15 (a), 3.65 (b), 4.17 (c) and 5.04 (d). The sample of kinetic curve with fitting curve (double exponential (e) and single exponential (f) for reaction carried out at pH = 3.65). Conditions: $C_{0,Pt(IV)}$ = 1.0 mM, $C_{0,\ H2Asc}$ = 60 mM, T = 313 ± 0.1 K, I = 0.06 M.

## S4. Kinetic curves at different ionic strength

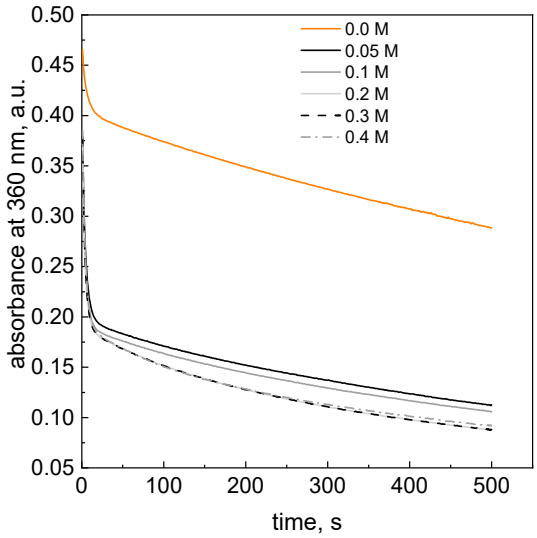



**Figure S4.** The sample of kinetic curve registered during Pt(IV) ion reduction using ascorbic acid. Conditions: $C_{0,Pt(IV)}$ = 1.0 mM, $C_{0,\ H2Asc}$ = 60 mM, T = 313 ± 0.1 K, pH = 2.5.

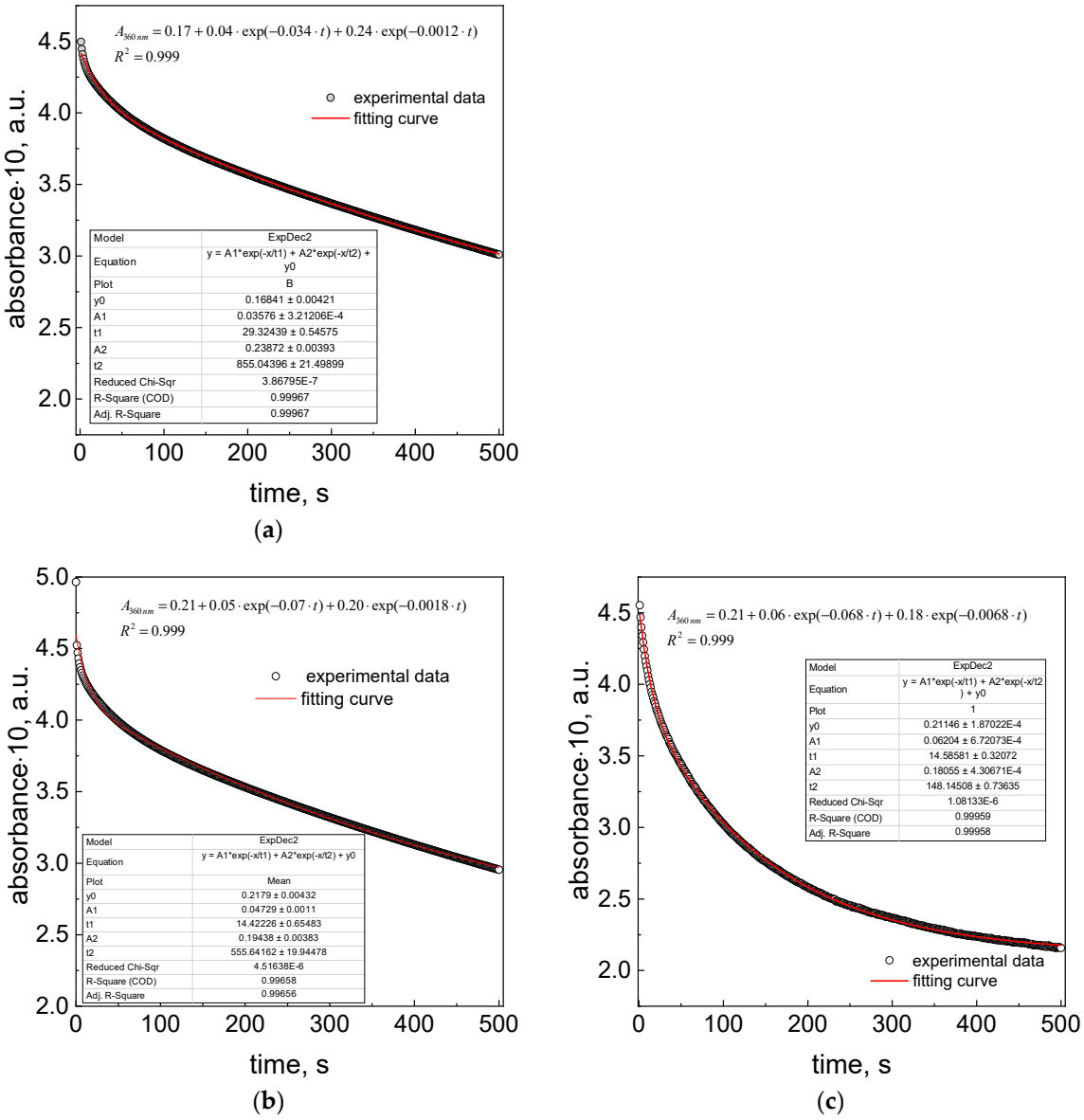
## S5. The influence of chloride concentration on the share of platinum species

**Table S1.** The influence of chloride ions concentration on the share of the platinum species. Conditions: $C_{0,Pt(IV)}$ = 1.00 mM, $C_{0,H2Asc}$ = 60.0 mM, [$Na^+$] = 0.4 M, T = 313 ± 0.1 K, pH = 2.50 ± 0.5, I = 0.4 M.

| $[Cl^-]$ M | $y_0 \propto C_{[PtCl_4]^{2-}}$ a.u. | $A_1 \propto C_{[PtCl_6]^{2-}}$ a.u. | $A_2 \propto C_{[PtCl_5(H_2O)]^-}$ a.u. | $C_{[PtCl_4]^{2-}}$, mM | $C_{[PtCl_6]^{2-}}$, mM | $C_{[PtCl_5(H_2O)]^-}$, mM |
|---|---|---|---|---|---|---|
| 0.0 | 0.067 | 0.18 | 0.14 | 1.12 | 0.367 | 0.285 |
| 0.05 | 0.025 | 0.14 | 0.19 | 0.446 | 0.286 | 0.388 |
| 0.10 | 0.03 | 0.2 | 0.16 | 0.536 | 0.408 | 0.326 |
| 0.20 | 0.03 | 0.25 | 0.15 | 0.536 | 0.510 | 0.306 |
| 0.30 | 0.04 | 0.26 | 0.135 | 0.714 | 0.531 | 0.276 |
| 0.40 | 0.05 | 0.27 | 0.13 | 0.893 | 0.551 | 0.265 |

$C_{[PtCl_6]^{2-}} = A_1/\varepsilon$, $C_{[PtCl_5(H_2O)]^-} = A_2/\varepsilon$, $C_{[PtCl_4]^{2-}} = y_0/\varepsilon_{Pt(II)}$, where ε = 490 $M^{-1}cm^{-1}$, $\varepsilon_{Pt(II)}$ = 56 $M^{-1}cm^{-1}$.

## S6. The influence of the oxygen on kinetic curves.




| Model | ExpDec2 |
|---|---|
| Equation | y = A1*exp(-x/t1) + A2*exp(-x/t2) + y0 |
| Plot | B |
| y0 | 0.16841 ± 0.00421 |
| A1 | 0.03576 ± 3.21206E-4 |
| t1 | 29.32439 ± 0.54575 |
| A2 | 0.23872 ± 0.00393 |
| t2 | 855.04396 ± 21.49899 |
| Reduced Chi-Sqr | 3.86795E-7 |
| R-Square (COD) | 0.99967 |
| Adj. R-Square | 0.99967 |

| Model | ExpDec2 |
|---|---|
| Equation | y = A1*exp(-x/t1) + A2*exp(-x/t2) + y0 |
| Plot | Mean |
| y0 | 0.2179 ± 0.00432 |
| A1 | 0.04729 ± 0.0011 |
| t1 | 14.42226 ± 0.65483 |
| A2 | 0.19438 ± 0.00383 |
| t2 | 555.64162 ± 19.94478 |
| Reduced Chi-Sqr | 4.51638E-6 |
| R-Square (COD) | 0.99658 |
| Adj. R-Square | 0.99656 |

| Model | ExpDec2 |
|---|---|
| Equation | y = A1*exp(-x/t1) + A2*exp(-x/t2) + y0 |
| Plot | 1 |
| y0 | 0.21146 ± 1.87022E-4 |
| A1 | 0.06204 ± 6.72073E-4 |
| t1 | 14.58581 ± 0.32072 |
| A2 | 0.18055 ± 4.30671E-4 |
| t2 | 148.14508 ± 0.73635 |
| Reduced Chi-Sqr | 1.08133E-6 |
| R-Square (COD) | 0.99959 |
| Adj. R-Square | 0.99958 |

**Figure S5.** The sample of kinetic curve with fitting registered during Pt(IV) ion reduction using ascorbic acid containing oxygen (a,b) and in deaerated solution (c). Conditions: $C_{0,Pt(IV)}$ = 1.0 mM, $C_{0,\ H2Asc}$ = 60 mM (a), 2.0 mM (b, c), T = 313 ± 0.1 K, I = 0.06 M, pH = 2.5.

**Table S2.** Experimental and calculated values of observed rate constants.

| **Solution** | Amount of reductant, mM | $k_{1,obs}$ $s^{-1}$ | $k_{2,\ obs}$ $s^{-1}$ | Degree of dissociation, $\alpha$[1], % |
|---|---|---|---|---|
| Contains $O_2$ | 60 mM | 0.034 | 0.0012 | 4 |
| | 2 mM | 0.07 | 0.0018 | 20 |
| Deaerated | 2 mM | 0.068 | 0.0068 | 20 |

[1] $\alpha, \% = \alpha \cdot 100\%$, where $\alpha = \sqrt{\frac{Ka}{C}}$, and Ka – dissociation constant for ascorbic acid ($K_a = 10^{-pK_a}$, $pK_a$ = 4.1) and equals $7.9 \cdot 10^{-5}$.

S7. Sample of kinetic curves registered at different wavelength

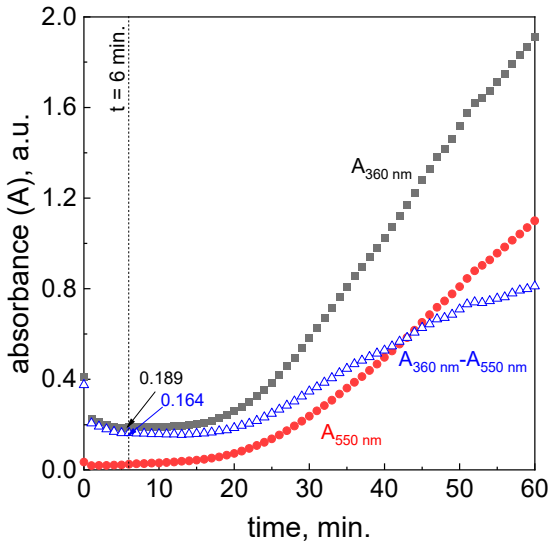



**Figure S6.** The sample of kinetic curves registered at two wavelength for process of Pt(IV) ion reduction using ascorbic acid and kinetic curve containing correction related to turbidity level ($A_{360\ nm}$-$A_{550\ nm}$). Conditions: $C_{0,Pt(IV)}$ = 1.0 mM, $C_{0,\ H2Asc}$ = 60 mM, T = 313 ± 0.1 K, I = 0.06 M, pH = 2.5.