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# A model of chronoamperometry of a two electrons electro-deposition reaction with the adsorption of intermediate

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### Abstract

*A single step chronoamperometry of reversible reactions complicated by the intermediate adsorption and the product deposition on inert electrodes is compared theoretically with an initial state of a simple two electrons electro-deposition. If the intermediate is highly unstable, these two mechanisms are similar, but the mechanism with successive electron transfers is needed to explain the responses appearing generally. The stability of intermediate depends on standard potentials of two steps and on the strength of adsorption. Two limiting cases are analysed and the difference between them is described.*

### Keywords

Two steps electrode mechanisms; adsorption of intermediate; logarithmic analysis; simultaneous electrons transfer; theory of electro-deposition reactions.

## Introduction

In electro-deposition reactions reactants are soluble, but products are insoluble in electrolyte and electrode [1-3]. These reactions are utilized in many technologies [4-6]. The product can be deposited onto a foreign substrate or onto the same pure product [7,8]. The soluble - insoluble electrochemical systems are similar to electro-adsorption reactions [9-12] and surface reactions [13,14]. If more than one electron is transferred in this reaction, they can be exchanged simultaneously or one after another [13-15]. There are opinions that the latter case is more probable [16]. This means that two electrons reductions must be explained by the EE mechanisms. In this paper the principle of successive electron transfers is applied to the electro-deposition reactions.

## Model

In the first mechanism the formation of solid deposit on an inert electrode is imagined as a two steps electro-reduction with the adsorption of intermediate. This process is presented by chemical equations (1) to (3):

$$Ox^{2+} + e^- \leftrightarrow Int^+ \tag{1}$$

$$Int^+ \longleftrightarrow Int^+_{ads} \tag{2}$$

$$Int^+_{ads} + e^- \longleftrightarrow Red_{dep} \tag{3}$$

It is assumed that the reactant and the intermediate are soluble species, but the final product is not. The later forms a monolayer of independent atoms or molecules in very low surface concentration. The same applies to the adsorbed intermediate. On the stationary planar electrode the diffusion and reversible reductions are defined by the differential equations and boundary conditions (4) – (15):

$$\frac{\partial c_{Ox}}{\partial t} = D\frac{\partial^2 c_{Ox}}{\partial x^2} \tag{4}$$

$$\frac{\partial c_{Int}}{\partial t} = D\frac{\partial^2 c_{Int}}{\partial x^2} \tag{5}$$

$$t=0, x\geq 0: \qquad c_{Ox}=c_{Ox}*, c_{Int}=0, \Gamma_{Int}=0, \Gamma_{Red}=0 \tag{6}$$

$$t>0, x\rightarrow\infty: \qquad c_{Ox}\rightarrow c_{Ox}*, c_{Int}\rightarrow 0 \tag{7}$$

$$x=0: \qquad D\left(\frac{\partial c_{Ox}}{\partial x}\right)_{x=0} = -\frac{I_1}{FS} \tag{8}$$

$$D\left(\frac{\partial c_{Int}}{\partial x}\right)_{x=0} = \frac{d\Gamma_{Int}}{dt} + \frac{I_1-I_2}{FS} \tag{9}$$

$$\frac{d\Gamma_{Red}}{dt} = -\frac{I_2}{FS} \tag{10}$$

$$\left(c_{Ox}\right)_{x=0} = \left(c_{Int}\right)_{x=0} e^{\varphi_1} \tag{11}$$

$$\varphi_1 = \frac{F}{RT}\left(E-E_1^{\,0}\right) \tag{12}$$

$$\Gamma_{Int} = \Gamma_{Red} e^{\varphi_2} \tag{13}$$

$$\varphi_2 = \frac{F}{RT}\left(E-E_2^{\,0}\right) \tag{14}$$

$$K_{ads}\left(c_{Int}\right)_{x=0} = \Gamma_{Int} \tag{15}$$

The meanings of symbols are the following: $c_z$ is a concentration of Z species, $c_{Ox}*$ is a bulk concentration of the reactant, $D$ is a common diffusion coefficient, $E$ is an electrode potential, $E_1^0$ and $E_2^0$ are standard potentials, $F$ is Faraday constant, $\Gamma_z$ is surface concentration of Z species, $I_1$ and $I_2$ are currents, $K_{ads}$ is the adsorption constant of linear isotherm, $R$ is gas constant, $S$ is electrode surface area, $t$ is time, $T$ is temperature and $x$ is a distance.

The differential equations (4) and (5) are solved for the single step chronoamperometry in which the potential is suddenly changed from the initial value, at which no reaction occurs, to the constant value at which the current is measured as a function of time. The method of Laplace transforms is used [17,18] and the details are reported in the Appendix. The solutions for dimensionless currents are given by equations (16) – (22):

$$\Phi_1 = -1 + \frac{e^{\varphi_1}\mathcal{F}\left(a\sqrt{t}\right)}{1+e^{\varphi_1}} \tag{16}$$

$$\Phi_2 = \frac{-1+\mathcal{F}\left(a\sqrt{t}\right)}{1+e^{\varphi_2}} \tag{17}$$

$$a = \frac{\left(1 + e^{\varphi_1}\right) e^{\varphi_2} \sqrt{D}}{K_{ads}\left(1 + e^{\varphi_2}\right)} \tag{18}$$

$$\mathcal{F}\left(a\sqrt{t}\right) = a\sqrt{\pi t}\, e^{a^2 t} \mathrm{erfc}\left(a\sqrt{t}\right) \tag{19}$$

$$\Phi_1 = \frac{I_1 \sqrt{\pi t}}{FS c_{Ox}{}^* \sqrt{D}} \tag{20}$$

$$\Phi_2 = \frac{I_2 \sqrt{\pi t}}{FS c_{Ox}{}^* \sqrt{D}} \tag{21}$$

$$\Phi = \Phi_1 + \Phi_2 \tag{22}$$

The functions of potential are characterized by the following limiting values:

$$\lim_{E \to \infty} a = \infty,\ \lim_{E \to -\infty} a = 0,\ \lim_{a\sqrt{t} \to 0} \mathcal{F}\left(a\sqrt{t}\right) = 0,\ \lim_{a\sqrt{t} \to \infty} \mathcal{F}\left(a\sqrt{t}\right) = 1,\ \lim_{E \to \infty} \Phi = 0\ \text{and}\ \lim_{E \to -\infty} \Phi = -2 .$$

In the second mechanism it is assumed that the deposit is formed by the concerted transfer of two electrons, as presented by eq.(23):

$$Ox^{2+} + 2e^- \leftrightarrow Red_{dep} \tag{23}$$

Under the same conditions as in the first mechanism the current can be calculated from the differential equation (4) and the boundary conditions (24) – (30):

$$t = 0,\ x \geq 0:\quad c_{Ox} = c_{Ox}{}^*,\ \Gamma_{Red} = 0 \tag{24}$$

$$t > 0,\ x \to \infty:\quad c_{Ox} \to c_{Ox}{}^* \tag{25}$$

$$x = 0:\quad D\left(\frac{\partial c_{Ox}}{\partial x}\right)_{x=0} = -\frac{I}{2FS} \tag{26}$$

$$\frac{d\Gamma_{Red}}{dt} = -\frac{I}{2FS} \tag{27}$$

$$k\left(c_{Ox}\right)_{x=0} = \Gamma_{Red}\, e^{\varphi_3} \tag{28}$$

$$\varphi_3 = \frac{2F}{RT}\left(E - E_3^0\right) \tag{29}$$

$$k = 1\ cm \tag{30}$$

The solution for chronoamperometry is given by equations (31) – (33):

$$\Psi = -1 + \mathcal{F}\left(b\sqrt{t}\right) \tag{31}$$

$$b = \frac{\sqrt{D}}{k}\, e^{\varphi_3} \tag{32}$$

$$\Psi = \frac{I\sqrt{\pi t}}{2FS c_{Ox}{}^* \sqrt{D}} \tag{33}$$

Equation (31) corresponds to the first part of electrodeposition current - time curve, before the minimum after which the nucleation develops [3,19,20]. The half-wave potential of the function $\Psi$ is defined by the equation: $\mathcal{F}(b\sqrt{t}) = 0.5$, which is satisfied if $b\sqrt{t} = 0.433$ and $E_{1/2} - E_3^0 =$ = $RT/2F$ (ln 0.433 + ln $k$ - ½ ln $D$ - ½ ln $t$). For the parameters used in the calculations ($D = 10^{-5}$ cm$^2$/s, $t = 1$ s, $k = 1$ cm and $RT/2F = 0.01285$) the half-wave potential is $E_{1/2} = E_3^0 + 0.063$ V.

In the third mechanism it is assumed that there is no adsorption of the intermediate. For this reason the boundary conditions of the differential equations (4) and (5) are changed in a way that the condition (15) is omitted because $K_{ads} = 0$, the term $d\Gamma_{Int}/dt$ is omitted in the condition (9) because $\Gamma_{Int} = 0$ and instead the condition (13) the Nernst equilibrium for the electro-adsorption reactions that is defined by eqs. (34) and (35) is introduced:

$$k\left(c_{Int}\right)_{x=0} = \Gamma_{Red}e^{\varphi_4} \tag{34}$$

$$\varphi_4 = \frac{F}{RT}\left(E - E_4^{\,0}\right) \tag{35}$$

The solutions given by equations (36) – (38) are obtained for the single pulse chronoamperometry:

$$\Phi = -2 + \frac{1+2e^{\varphi_1}}{1+e^{\varphi_1}}\mathcal{F}\left(d\sqrt{t}\right) \tag{36}$$

$$d = \frac{\sqrt{D}}{k}e^{\varphi_4}\left(1+e^{\varphi_1}\right) \tag{37}$$

$$\Phi = \frac{\left(I_1+I_2\right)\sqrt{\pi t}}{FSc_{Ox}^{*}\sqrt{D}} \tag{38}$$

In the final mechanism it is assumed that the intermediate cannot exist in the dissolved form but only if immobilized at the electrode surface. This may apply to some cation radicals that are stabilized by the electrons of the electrode material [21]. The differential equation (4) is solved by using the boundary conditions (6)-(8), (10), (13) and (14) together with the conditions (39) – (41):

$$k\left(c_{Ox}\right)_{x=0} = \Gamma_{Int}e^{\varphi_5} \tag{39}$$

$$\varphi_5 = \frac{F}{RT}\left(E - E_5^0\right) \tag{40}$$

$$\frac{d\Gamma_{Int}}{dt} = -\frac{I_1}{FS} + \frac{I_2}{FS} \tag{41}$$

The solution is given by equations (42) and (43):

$$\Phi = -\frac{2+e^{\varphi_2}}{1+e^{\varphi_2}}\left(1 - \mathcal{F}\left(g\sqrt{t}\right)\right) \tag{42}$$

$$g = \frac{\sqrt{D}e^{\varphi_5}e^{\varphi_2}}{k\left(1+e^{\varphi_2}\right)} \tag{43}$$

Experimentally, the chronoamperometric conditions can be achieved in the normal pulse voltammetry because during the period between pulses the product and intermediate are oxidized and the reactant is regenerated [22].

## Results and discussion

A result of a single step chronoamperometric measurement is a current - time relationship at a certain potential. If the time is constant and the potential is changed from one to another measurement, the dependence of current on potential resembles a polarographic wave. Some examples are shown in Figure 1 for various differences between standard potentials of the first and the second electron transfers. The dimensionless current is defined by eq. (22). The wave is steeper and its half-wave potential is higher if the difference $E_2^0 - E_1^0$ is increased. The apparent number of

electrons exchanged in the reaction can be estimated from the logarithmic analyses of the waves that are shown in Figure 1B. The logarithm of the ratio $\Phi / (\Phi_{lim} - \Phi)$ is a function of electrode potential and this relationship is a curve with either one or two asymptotes. If $E_2^0 = E_1^0$ the slope $\Delta \log(\Phi / (\Phi_{lim} - \Phi))/\Delta(E - E_1^0)$ is equal to -16.905 V$^{-1}$ if $\log(\Phi / (\Phi_{lim} - \Phi)) > 1$ and to -16.921 V$^{-1}$ if $\log(\Phi / (\Phi_{lim} - \Phi)) < -1$.
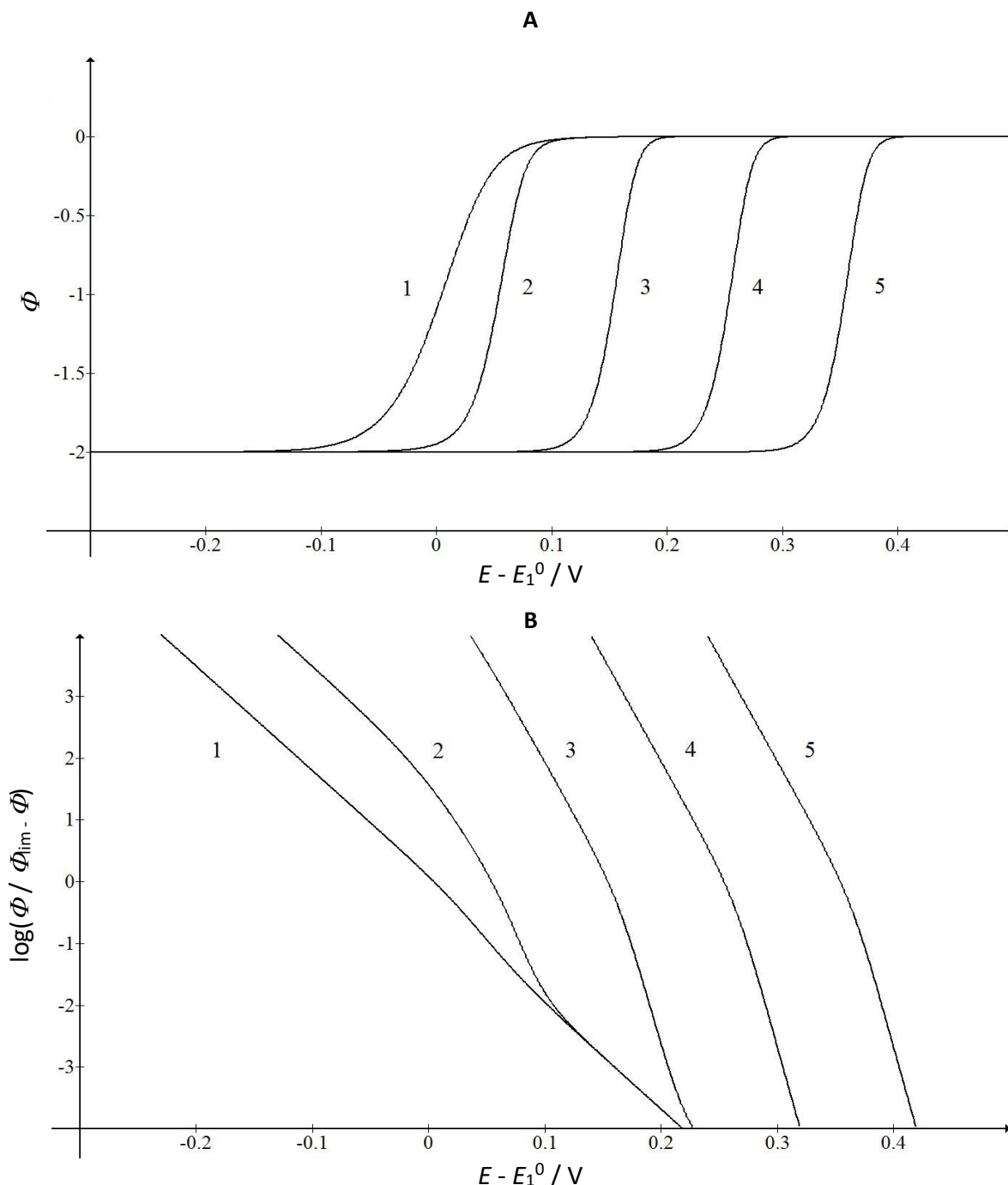


***Figure 1.*** *Polarograms of EE mechanism with the intermediate adsorption and the product deposition on the inert electrode (A) and their logarithmic analyses (B). K$_{ads}$ =0.1 mm, t = 1 s, D = 10$^{-5}$ cm$^2$ s$^{-1}$ and E$_2^0$ -E$_1^0$ =  0.0 (1), 0.1 (2), 0.3 (3), 0.5 (4) and 0.7 (5) V*

The inverse values of these slopes are -0.0592 V and -0.0591 V, which are equal to -2.303 $RT / F$ and correspond to the single electron transfer. If $E_2^0 - E_1^0 = 0.1$ V the lower slope is the same, but the upper one is -16.981 V$^{-1}$ and its inverse value is -0.0589 V, which still corresponds to the single electron. Curve 2 in Figure 1B shows that the logarithmic analysis between asymptotes is steeper

than the asymptotes. If $E_2^0 - E_1^0 \geq 0.3$ V the lower asymptote vanishes while the slopes of upper one decrease to -29.556 $V^{-1}$ (3), -33.712 $V^{-1}$ (4) and -33.81 $V^{-1}$ (5). The inverse value of the last slope is -0.0296 V, which is equal to -2.303 $RT / 2F$ and corresponds to the transfer of two electrons. The logarithmic analysis of eq. (31) is the curve with the slope of the upper asymptote of -33.8 $V^{-1}$, the inverse value of which is -0.0296 V. This shows that the response of the EE mechanism is equal to the two electrons wave if $E_2^0 - E_1^0 \geq 0.5$ V.
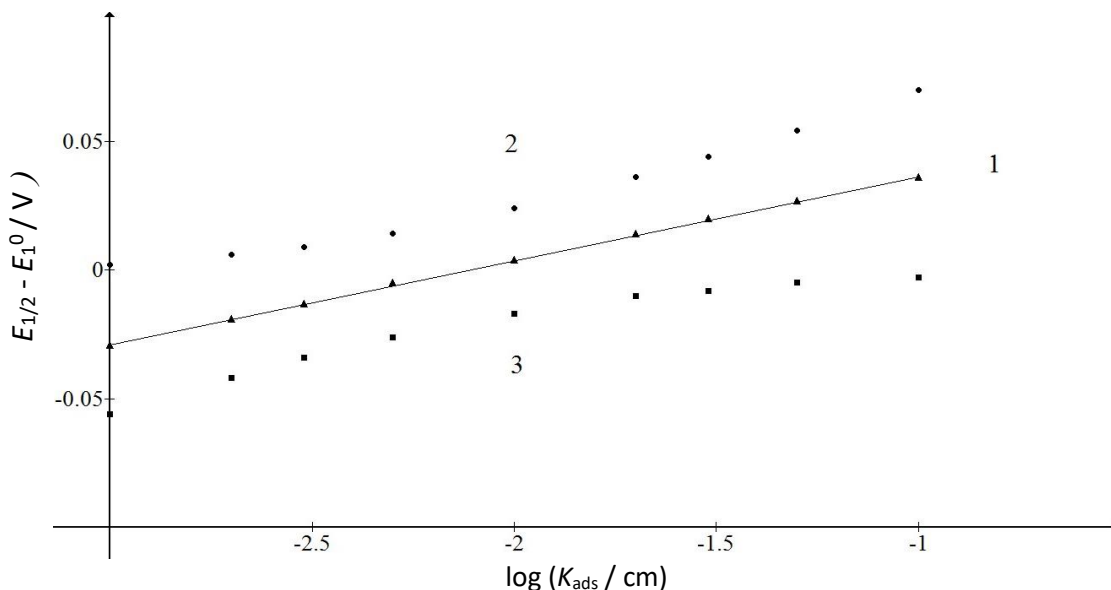


**Figure 2.** *Dependence of half-wave potentials of EE mechanism (1) and its first (2) and the second components (3) on the logarithm of adsorption constant;* $E_2^0 = E_1^0$ . *All other data are as in Fig. 1.*
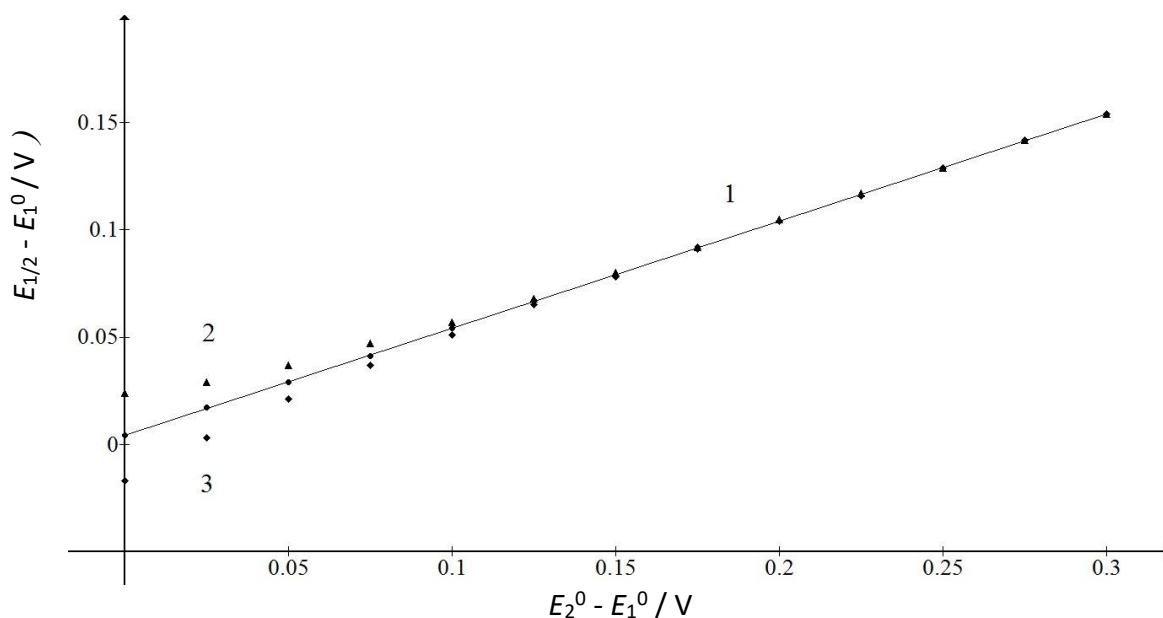


**Figure 3.** *Dependence of half-wave potentials of EE mechanism (1) and its first (2) and the second components (3) on the difference between standard potentials of the second and the first electron transfers;* $K_{ads} = 0.1$ *mm. All other data are as in Fig. 1*

Figures 2 and 3 show the half-wave potentials of the polarogram of EE mechanism and of its components $\Phi_1$ and $\Phi_2$ as the functions of the logarithm of adsorption constant and the difference between standard potentials $E_2^0$ and $E_1^0$. All three potentials increase with the increasing influence of adsorption: the one of the first component changes from 0.002 to 0.070 V while that of the

second one changes from -0.056 to -0.003 V. In the vicinity of $K_{ads}$ = 0.1 mm there is the relationship: $E_{1/2.EE} = (E_{1/2.1} + E_{1/2.2}) / 2$, while in the whole interval $E_{1/2.EE}$ satisfies the equation (44):

$$E_{1/2,EE} - E_1^0 = 0.0325 \log K_{ads} + 0.0685 \text{ V} \tag{44}$$

The potentials $E_{1/2.1}$ and $E_{1/2.2}$ of the components of curve 1 in Fig. 1A are equal to 0.024 and -0.016 V, respectively, and $E_{1/2.EE}$ is equal to 0.004 V *vs.* $E_1^0$. The difference between half-wave potentials of components decreases with the increasing difference $E_2^0 - E_1^0$, which can be seen in Fig. 3. The half-wave potential of EE mechanism is defined by the linear relationship (45):

$$E_{1/2,EE} - E_1^0 = \frac{E_2^0 - E_1^0}{2} + 0.004 \text{ V} \tag{45}$$

The intercept depends on the adsorption constant and if $K_{ads}$ = 0.01 mm, the intercept is equal to -0.029 V.

The last two equations can be used to correlate the standard potentials $E_1^0$, $E_2^0$ and $E_3^0$ that are defined by equations (12), (14) and (29). The half-wave potential of the response of the second mechanism (eq. 31) satisfies the equation (46):

$$E_{1/2,2e} - E_3^0 = \frac{RT}{2F}\left( \ln 0.433 - \frac{1}{2}\ln Dt \right) \tag{46}$$

In Figure 1B it is demonstrated that logarithmic analyses of responses of the first and the second mechanisms are identical if $E_2^0 = E_1^0 \geq 0.5$ V. So, one can assume that half-wave potentials of these responses are also identical: $E_{1/2.2e} - E_{1/2.EE}$. If it is true, the third standard potential is equal to:

$$E_3^0 = E_1^0 + \frac{E_2^0 - E_1^0}{2} - \frac{RT}{2F}\left( \ln 0.433 - \frac{1}{2}\ln Dt \right) + 0.0325 \ \log K_{ads} + 0.0685 \text{ V} \tag{47}$$
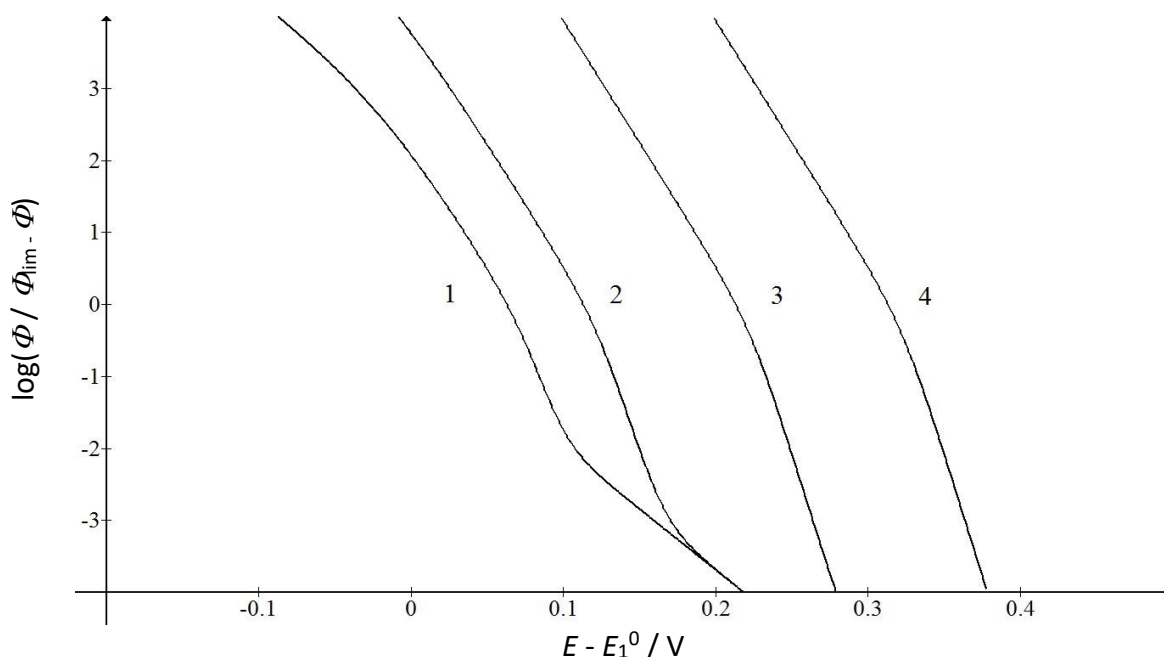


**Figure 4.** *Logarithmic analyses of EE mechanism with the product deposition on the inert electrode; $E_4^0 - E_1^0$ = 0 (1), 0.1 (2), 0.3 (3) and 0.5 (4) V. All other data are as in Fig. 1*

Figure 4 shows logarithmic analyses of polarograms of the third mechanism. If $E_4^0 = E_1^0$ the slopes of the upper and the lower asymptotes are -17.995 and -16.903 V$^{-1}$, respectively, which both correspond to the transfer of one electron. The upper slope of curve 2 is -33.03 V$^{-1}$, the inverse value of which is -0.0303 V, while the lower slope is the same as the one in the curve 1. The upper slopes

of curves 3 and 4 are -33.636 and -33.826 V$^{-1}$, which both correspond to the transfer of two electrons. The half-wave potentials satisfy the relationship (48):

$$E_{1/2,EE} - E_1^0 = \frac{E_4^0 - E_1^0}{2} + 0.063 \text{ V} \quad \text{V} \tag{48}$$

Figure 4 shows that in the absence of adsorption of intermediate the response of EE mechanism resembles the response of concerted transfer of two electrons if the difference in standard potentials of the second and the first electron transfers is equal or higher than 0.3 V, which is lower than in Figure 1. The opposite effect can be seen in Figure 5. Under the influence of immobilization of intermediate the upper slope of curves 1 and 2 is -16.904 V$^{-1}$ and the lower slope is -33.794 V$^{-1}$. The upper slopes of curves 4 and 5 are -33.11 V$^{-1}$ and -33.797 V$^{-1}$, respectively. So, the EE response resembles the two electrons transfer if $E_2^0 - E_5^0 \geq 0.7$ V, which is higher than in Figure 1. However, if $E_2^0 - E_5^0 \leq 0.1$ V the logarithmic analysis indicates the transfer of both the single electron and two electrons. The half-wave potentials are given by the equation (49):

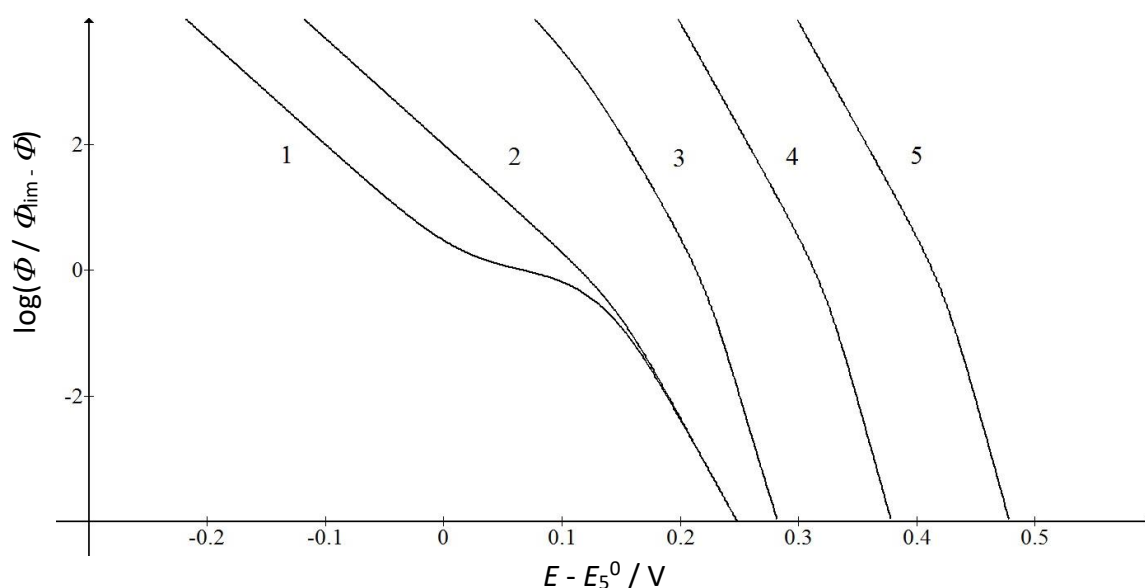$$E_{1/2,EE} - E_5^0 = \frac{E_2^0 - E_5^0}{2} + 0.063 \text{ V} \tag{49}$$



**Figure 5.** *Logarithmic analyses of EE mechanism with the intermediate immobilization and the product deposition on the inert electrode;* E$_2^0$ - E$_5^0$ = 0 (1), 0.1 (2), 0.3 (3), 0.5 (4) and 0.7 (5) V. *All other data are as in Fig. 1*

In eq. (39) the unknown numerical value of the auxiliary constant $k = 1$ cm is contained by the standard potential $E_5^0$. For this reason, $E_5^0$ is not equal to $E_1^0$. The same applies to eq. (34) and $E_4^0$ that is different from $E_2^0$.

The adsorption of intermediate seems as a logical step in the formation of solid deposit because it enables a gradual transition between electrode reaction of dissolved species and the reaction of surface confined species. In the other three mechanisms the mixed electrode reactions involving one dissolved and one confined species appear. As the strength of adsorption may vary from very weak to very strong, the third and the fourth mechanisms can be considered as the limiting cases of the first one. The calculations show that all three mechanisms tend to the second one if the intermediate is highly unstable. The biggest differences between them appear at equal standard potentials of two steps. In the absence of adsorption the slopes of logarithmic analyses suggest that only one electron is transferred, but if the intermediate is immobilized at the electrode surface the

slopes of this analysis correspond to the transfer of both a single electron and a pair of electrons. Electrodeposition and stripping of metal ions generally appear as the concerted electrons transfers, but the influence of electro-inactive surface active substances indicates that they might be multi steps mechanisms [23,24].

## Conclusions

An EE mechanism with the adsorption of intermediate and the deposition of product is a good representation of a two electrons electro-deposition reaction. The stability of intermediate can be estimated by the logarithmic analysis of the polarogram. The inverse value of the slope of the upper part of this curve indicates that either one or two electrons are transferred. The first case appears if the difference between standard potentials of two steps is low and the other case corresponds to the high difference and unstable intermediate. In the first case logarithmic analysis may depend on the strength of adsorption because it is an additional stabilizer of the intermediate. Particularly is interesting the response to the immobilization of intermediate because this mechanism can be recognized by two different slopes of the upper and lower parts of logarithmic analysis. Half-wave potentials of polarograms depend on standard potentials of various mechanisms. Polarogram caused by the concerted transfer of two electrons is a limiting response of all three investigated EE mechanisms. However, they may be operative under the conditions of higher stability of intermediate. The electro-deposition is a complex process that includes an accumulation in the second and higher layers and a nucleation and a crystallization, but the initial state described in this paper defines the basic thermodynamic relationships at the constant potential. If this process is analysed as an EE mechanism, the reactions of intermediate appear as additional variables that cannot be neglected generally.

## Appendix

The application of Laplace transforms method on the differential equations (4) and (5) and the initial and boundary conditions (6)-(15) leads to the solutions in the Laplace space that are given by equations (50) and (51):

$$\mathcal{L}c_{Ox} = \frac{c_{Ox}{}^{*}}{s} + \frac{e^{-xD^{-1/2}s^{1/2}}}{\sqrt{s}}\mathcal{L}\frac{I_1}{FSD^{1/2}} \tag{50}$$

$$\mathcal{L}c_{Int} = e^{-xD^{-1/2}s^{1/2}}\left(-\frac{\sqrt{s}}{\sqrt{D}}\mathcal{L}\Gamma_{Int} + \frac{1}{\sqrt{s}}\mathcal{L}\frac{I_2}{FSD^{1/2}} - \frac{1}{\sqrt{s}}\mathcal{L}\frac{I_1}{FSD^{1/2}}\right) \tag{51}$$

Considering that the electrode potential is constant, the Nernst equations (11) and (13) can be directly transformed into Laplace space and the currents in this space are defined by equations (52) and (53):

$$\mathcal{L}\frac{I_1}{FS\sqrt{D}c_{Ox}{}^{*}} = -\frac{1}{\sqrt{s}+a} - \frac{a}{\left(1+e^{\varphi_1}\right)\left(\sqrt{s}+a\right)\sqrt{s}} \tag{52}$$

$$\mathcal{L}\frac{I_2}{FS\sqrt{D}c_{Ox}{}^{*}} = -\frac{1}{\left(1+e^{\varphi_2}\right)\left(\sqrt{s}+a\right)} \tag{53}$$

The parameter *a* is defined by eq. (18). The inverse transformations of eqs. (52) and (53) give the equations (16) and (17). The currents depend on the potential and time. Usually the current is measured at the end of pulse and the potential of pulse is changed from one measurement to the

other. In this way a series of current - potential points is obtained that can be interconnected for the better graphical presentation. One can also measure the current flowing during the pulse at a constant potential, but for the initial period of the complex mechanism the pulse duration must be very short and it is better to analyse the current - potential relationship. Under this condition the influence of various geometry of electrodes is minimal. Regarding the concentrations of electroactive species during the pulse, they can be calculated from equations (50)-(53) and the second Nernst equation.

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