Modelling a cyclic staircase voltammetry of two electron transfers coupled by a chemical reaction on a rotating disk electrode[•]

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Abstract: Two electrode reactions that are coupled by a chemical reaction are called an ECE mechanism. The model of this mechanism which has an unstable intermediate is developed for staircase voltammetry on the rotating disk electrode. It is assumed that both electrode reactions are fast and reversible and that the chemical reaction may appear to be of the second order and reversible. The influence of the concentration of an electro-inactive component of the chemical reaction is investigated, and the conditions under which the reaction turns into the first order one, and becomes totally irreversible, are reported.

Keywords: an ECE mechanism; steady-state response; logarithmic analysis; kinetic currents.

INTRODUCTION

The electrochemical reactions of *p*-nitrosophenol,[1,2] adriamycin,[3] benzenesulfonyl fluoride,[4,5] hexacyanochromate(III),[6] tocopherol,[7] methylcatechol[8,9] and dopamine[10] consist of two electron transfers that are coupled by a chemical reaction between the product of the first electrode reaction and the reactant of the second one.[11–13] The acronym of this mechanism is ECE and its theory is developed for both polarography[14–19] and voltammetry,[20–27] on either expanding or stationary planar and spherical electrodes. Depending on the difference between standard potentials of two electrode reactions, the response of ECE mechanism may consist of either two waves or a single wave.[28] This mechanism can be considered as a special case of multiple electron transfer reactions, with coupled chemical processes that are described by the extended schemes of squares.[29–32] Under the steady state conditions on the rotating disk electrodes the kinetics of chemical reaction in the ECE mechanism can be measured.[33–37] In this paper the

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theory of ECE is extended to the general case of the unstable intermediate in cyclic staircase voltammetry on the rotating disk electrode.

MODEL

It is assumed that an electrolytic solution contains a dissolved reactant of the first electrode reaction and an electro-inactive substance Y that cannot react with the mentioned reactant. The first electron transfer is a fast and reversible electro-oxidation. Its product cannot participate in the second electron transfer, but it can react with the substance Y to produce a new electroactive compound G that can be oxidized to the final product H. The standard potentials of the first and the second electrode reactions are equal, or the one of the second reaction is lower. Hence, the second reactant G is oxidized at the same potentials as the initial reactant A. Both chemical reaction and the second electrode reaction are reversible in the chemical and electrochemical senses, respectively. The described mechanism can be represented by the following chemical equations:

$$A \leftrightarrows B + e^- \tag{1}$$

$$B + Y \leftrightarrows G \tag{2}$$

$$G \leftrightarrows H + e^- \tag{3}$$

On the rotating disk electrode the mass transfer and currents are defined by the following system of differential equations and the initial and boundary conditions:

$$\frac{\partial c_A}{\partial t} = D\frac{\partial^2 c_A}{\partial x^2} - v\frac{\partial c_A}{\partial x} \tag{4}$$

$$\frac{\partial c_B}{\partial t} = D\frac{\partial^2 c_B}{\partial x^2} - v\frac{\partial c_B}{\partial x} - k_f c_B c_Y + k_b c_G \tag{5}$$

$$\frac{\partial c_Y}{\partial t} = D\frac{\partial^2 c_Y}{\partial x^2} - v\frac{\partial c_Y}{\partial x} - k_f c_B c_Y + k_b c_G \tag{6}$$

$$\frac{\partial c_G}{\partial t} = D\frac{\partial^2 c_G}{\partial x^2} - v\frac{\partial c_G}{\partial x} + k_f c_B c_Y - k_b c_G \tag{7}$$

$$\frac{\partial c_H}{\partial t} = D\frac{\partial^2 c_H}{\partial x^2} - v\frac{\partial c_H}{\partial x} \tag{8}$$

$$t = 0, x \geq 0 : c_A = c_A^*, c_B = 0, c_Y = c_Y^*, c_G = 0, c_H = 0 \tag{9}$$

$$t > 0, x \to \infty : c_A \to c_A^*, c_B \to 0, c_Y \to c_Y^*, c_G \to 0, c_H \to 0 \tag{10}$$

$$x = 0 : c_{B,x=0} = c_{A,x=0}\exp(F(E - E_1^0)/RT) \tag{11}$$

$$c_{H,x=0} = c_{G,x=0}\exp(F(E - E_2^0)/RT) \tag{12}$$

$$D(\frac{\partial c_A}{\partial x})_{x=0} = \frac{I_1}{FS} \tag{13}$$

$$D(\frac{\partial c_B}{\partial x})_{x=0} = -\frac{I_1}{FS} \tag{14}$$

$$D(\frac{\partial c_Y}{\partial x})_{x=0} = 0 \tag{15}$$

$$D(\frac{\partial c_G}{\partial x})_{x=0} = \frac{I_2}{FS} \tag{16}$$

$$D\left(\frac{\partial c_\mathrm{H}}{\partial x}\right)_{x=0} = -\frac{I_2}{FS} \qquad (17)$$

$$v = -0.510\omega^{3/2}\nu^{-1/2}x^2 \qquad (18)$$

$$K = \frac{k_\mathrm{f}}{k_\mathrm{b}} \qquad (19)$$

The meanings of all symbols are reported in Table I.

TABLE 1. The meanings of symbols

Symbol	Meaning
c_Z	Concentration of species Z
$c_\mathrm{A}^*, c_\mathrm{Y}^*$	Bulk concentrations of species A and Y
D	Diffusion coefficient
δ	Diffusion layer thickness
ΔE	Potential increment
Δt	Time increment
Δx	Space increment
E	Potential
E_1^0, E_2^0	Standard potentials
F	Faraday constant
I_1, I_2	Currents
ν	Kinematic viscosity
$k_\mathrm{f}, k_\mathrm{b}$	Rate constants of chemical reaction
K	Equilibrium constant of chemical reaction
ω	Rotation rate
R	Gas constant
S	Electrode surface area
t	Time
T	Temperature
τ	Step duration
v	Flow rate of solution

The Eqs. (4)–(8) were solved by the finite difference method.[38] The current was calculated for the staircase cyclic voltammetry. The dimensionless current is defined by the following equations:

$$\Phi = (I_1 + I_2)\delta_\mathrm{SS} / FSc_A^*D \qquad (20)$$

$$\delta_\mathrm{SS} = 1.61D^{1/3}\nu^{1/6}\omega^{-1/2} \qquad (21)$$

The following parameters were not changed: $D = 10^{-5}$ cm²/s, $\nu = 10^{-2}$ cm²/s, $\Delta t = 10^{-5}$ s, $D\Delta t/\Delta x^2 = 0.2$, $\Delta E = 1$ mV and $\tau = 10$ ms.

RESULTS AND DISCUSSION

An ECE mechanism can be recognized by performing the electrochemical experiments in the absence and the presence of the electro-inactive compound Y if it is possible. An imaginary response is presented in Fig. 1 for the reversible and
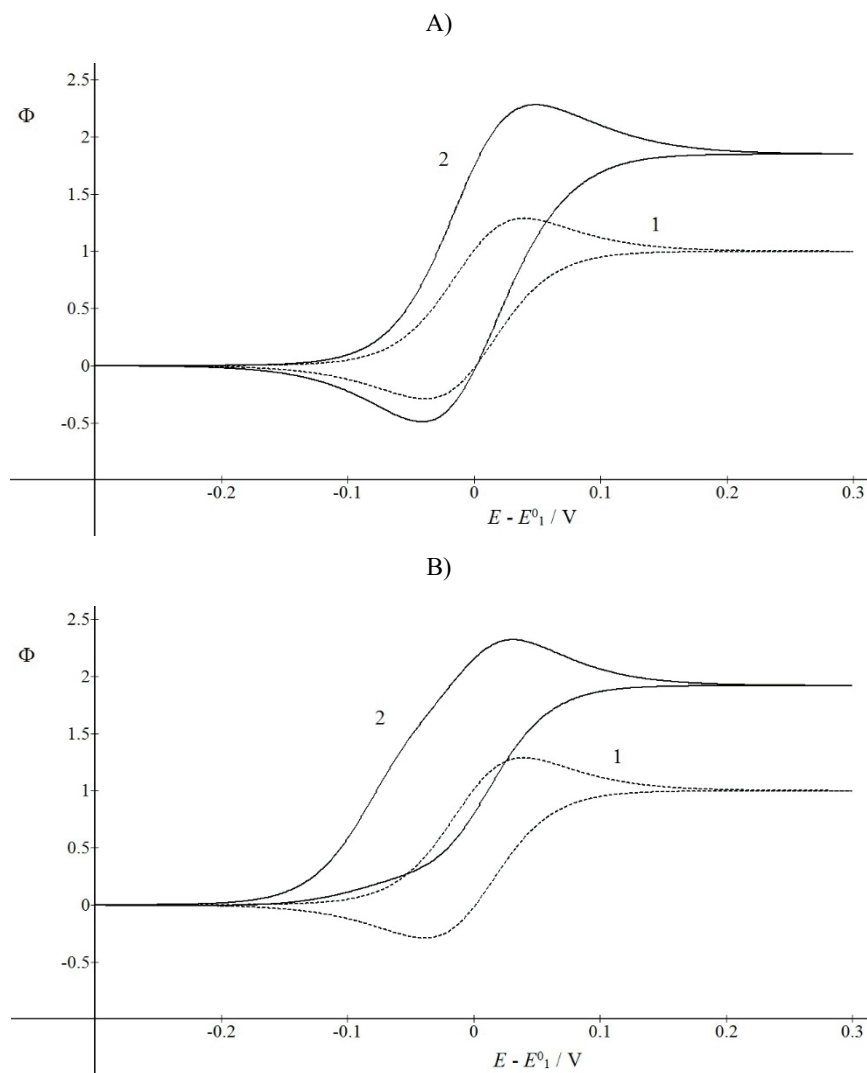
A)

B)

Fig. 1. Dimensionless cyclic staircase voltammograms of the ECE mechanism on the rotating disk electrode. $E_1^0 = E_2^0$, $D = 10^{-5}$ cm^2/s, $\nu = 10^{-2}$ cm^2/s, $\Delta t = 10^{-5}$ s, $D\Delta t/\Delta x^2 = 0.2$, $\Delta E = 1$ mV and $\tau = 10$ ms, $\omega = 4\pi$ rad/s, $k_f c_A^* = 10^3$ s^{-1}, $Kc_A^* = 1$ (A) and 10^3 (B) and $c_Y^* / c_A^* = 0$ (1) and 1 (2).

irreversible chemical reactions. It is also assumed that the standard potentials of the first and the second electrode reactions are equal and that both reactions are electrochemically reversible, as well as that the rotation rate of the disk electrode is rather low. In the absence of Y the voltammogram is characterised by the limiting current that is determined by the single electron transfer and the concentration of the initial reactant A (see Eq. (20)). Dimensionless peak currents ($\Phi_{p,ox}$

= 1.29 and $\Phi_{p,red}$ = –0.29) appear at 0.039 V and –0.039 V *vs.* E_1^0, respectively. If the bulk concentrations of A and Y are equal, the dimensionless limiting current increases to 1.74, which can be explained by the increasing number of exchanged electrons, and the peak currents depend on the dimensionless equilibrium constant Kc_A^*. The chemical reaction is reversible if Kc_A^* = 1 and irreversible if Kc_A^* = 10^3. In the first case, the peak currents of the oxidation and reduction are equal to 2.28 and –0.49, respectively, and the peak potentials are 0.048 V and –0.042 V *vs.* E_1^0. The rate of chemical reaction depends on the product $k_f c_A^*$ and the value assumed in Fig. 1 corresponds to a rather fast reaction that can transform the second reactant G into the first product B, in the reverse branch of the voltammogram. This is the origin of the reduction peak at –0.042 V. However, if Kc_A^* = 10^3 the backward rate constant of the chemical reaction is very small and the second voltammogram in Fig. 1B exhibits the oxidation peak at 0.031 V, but there is no reduction peak in the reverse branch. This form of the response is the indication of an irreversible chemical reaction in the ECE mechanism.

Fig. 2 shows the voltammograms influenced by the decreasing stability of the intermediate G. If $E_2^0 - E_1^0$ = –0.1 V, the second reactant G is oxidized at the electrode surface as soon as it is produced by the chemical reaction, and the response shows some characteristics of the concerted transfer of two electrons. Comparing to the curve 1, the oxidative maximum is higher and the reductive minimum is deeper, while the peak separation decreases from 90 to 67 mV and the median of peak potentials of curve 2 is –0.043 V *vs.* E_1^0, which is close to $(E_2^0 + E_1^0)/2$ that is predicted for infinitely fast chemical reaction.[39] However
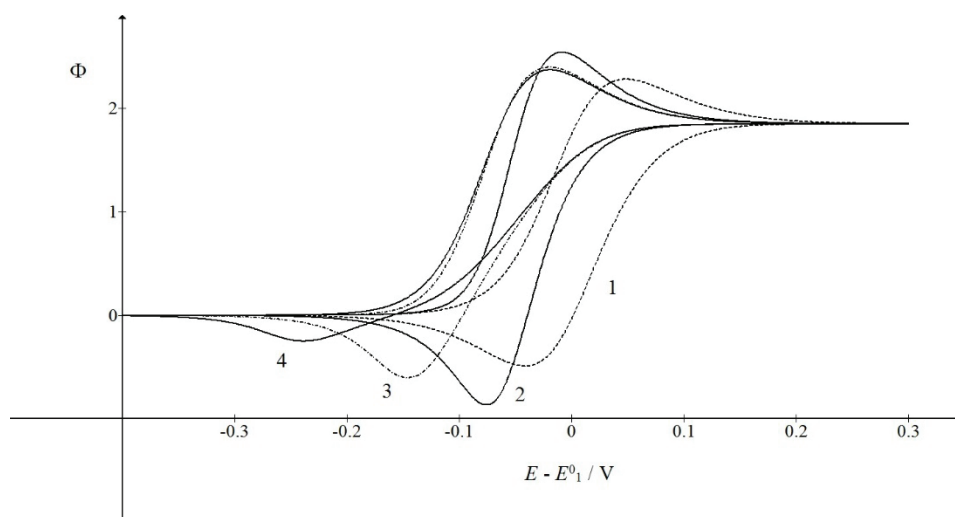

Fig. 2. Dependence of the ECE response on the second standard potential. Kc_A^* = 1, $c_Y^* = c_A^*$ and $(E_2^0 - E_1^0)/V$ = 0 (1), –0.1 (2), –0.2 (3) and –0.3 (4). All other parameters are as in Fig. 1.

the further decreasing of the difference $E_2^0 - E_1^0$ causes the diminishing of the reductive peak in the reverse branch of the voltammograms. Although the medians of peak potentials of curves 3 and 4 are –0.083 and –0.130 V, the peak separation increases to 126 and 220 mV, respectively. This is caused by the diffusion of the final product during the reverse scan, as can be seen in Fig. 3. Depending on the second standard potential, the peak potential of reduction of H is lower than –0.042 V, and more time is needed to reach it. During this time the concentration of H near the electrode surface is diminished and lower current is obtained by its reduction. This is another reason why the ECE may appear irreversible.
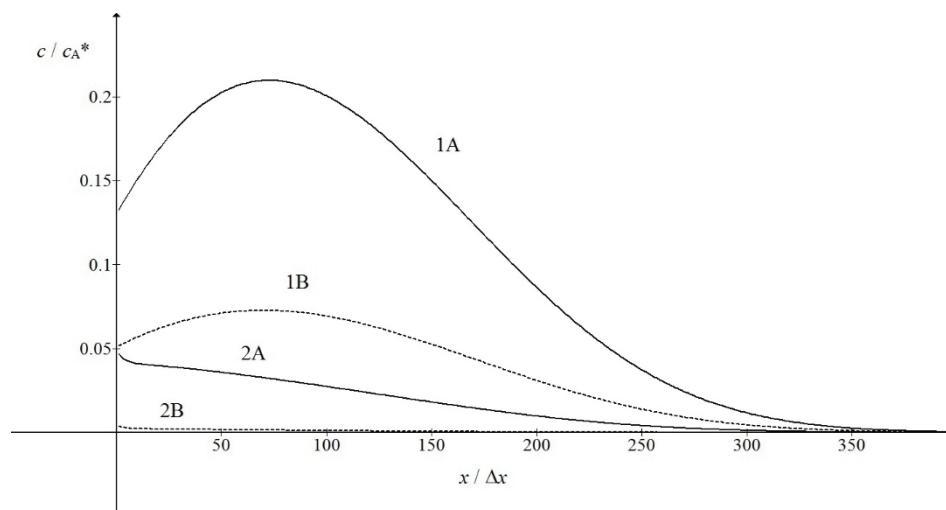

Fig. 3. Dimensionless concentrations of the final product H (1) and the second reactant G (2) during the reverse scan in cyclic voltammetry at –0.076 V (A) and –0.239 V (B).
$(E_2^0 - E_1^0)$ / V = –0.1 (A) and –0.3 (B). All other parameters are as in Fig. 2.

Under the influence of the increasing rotation rate, the maximum and minimum of the voltammogram of ECE mechanism gradually vanish and the response acquires the form of polarographic wave. This is shown in Fig. 4. The half-wave potential of the oxidative branch of polarogram is –0.003 V *vs.* E_1^0 and the one of the reductive reverse branch is 0.003 V. This difference appears because the calculated response corresponds to the near steady-state conditions. At lower scan rates the two branches are overlapped and $E_{1/2} - E_1^0 = 0$ V for equal diffusion coefficients. The limiting current of polarogram is lower than the limiting current of voltammogram, because the reactants spend more time near the electrode surface if the rotation rate is lower. Hence, the chemical reaction appears faster at lower rotation rate.

Fig 5 describes the logarithmic analyses of the oxidative branches of steady state voltammograms that correspond to various standard potentials of the second

electrode reaction. If $E_2^0 = E_1^0$ and chemical reaction is reversible this function is a straight line with the slope of the inverse function $\Delta(E - E_1^0) / \Delta \log(\Phi / (\Phi_{lim} - \Phi)) = 0.062$ V and $E_{1/2} - E_1^0 = -0.003$ V. So, the two parallel single electron transfers appear as a simple one electron wave. If $E_2^0 - E_1^0 = -0.1$ V this analysis is a curve with two parallel asymptotes and a steeper middle part. The inverse slope in the middle is 0.044 V and the one of asymptotes is 0.062 V. This is in the agreement with the theory of a simple EE mechanism with an unstable intermediate.[39] The half-wave potential is –0.041 V, which is close to the medium value of the peak potentials of curve 2 in Fig. 2. The half-wave potentials of the curves 3 and 4 in Fig. 5A are –0.054 and –0.055 V, respectively. This is similar to the potentials of maxima of curves 3 and 4 in Fig. 2, which are –0.020 and –0.019 V, respectively. This shows that the oxidation of the second reactant G can start only after the first reactant A is oxidized, regardless of the standard potential of the second electrode reaction.
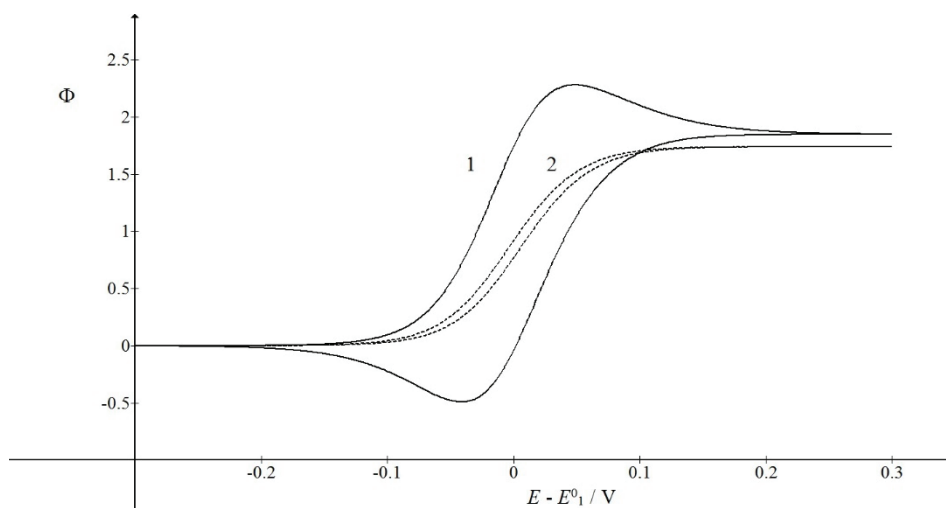

Fig. 4. Influence of the electrode rotation rate on the ECE responses. $E_2^0 = E_1^0$ and $\omega / $ rad s$^{-1} = 4\pi$ (1) and 40π (2). All other parameters are as in Fig. 2.

The logarithmic analyses of the ECE waves that are influenced by the irreversible chemical reaction are shown in Fig. 5B. If both standard potentials are equal, the slope in the middle is lower than the slopes of the asymptotes and the half-wave potential is –0.030 V $vs.$ E_1^0. The chemical reaction is consuming the first product B, and the whole ECE response appears at lower potential. Also, a small separation of the two electron transfers can be noted. If $E_2^0 - E_1^0 = -0.1$ V the logarithmic analysis acquires a regular form and the half-wave potential i –0.060 V. This is because the mechanism becomes irreversible.

A)

B)
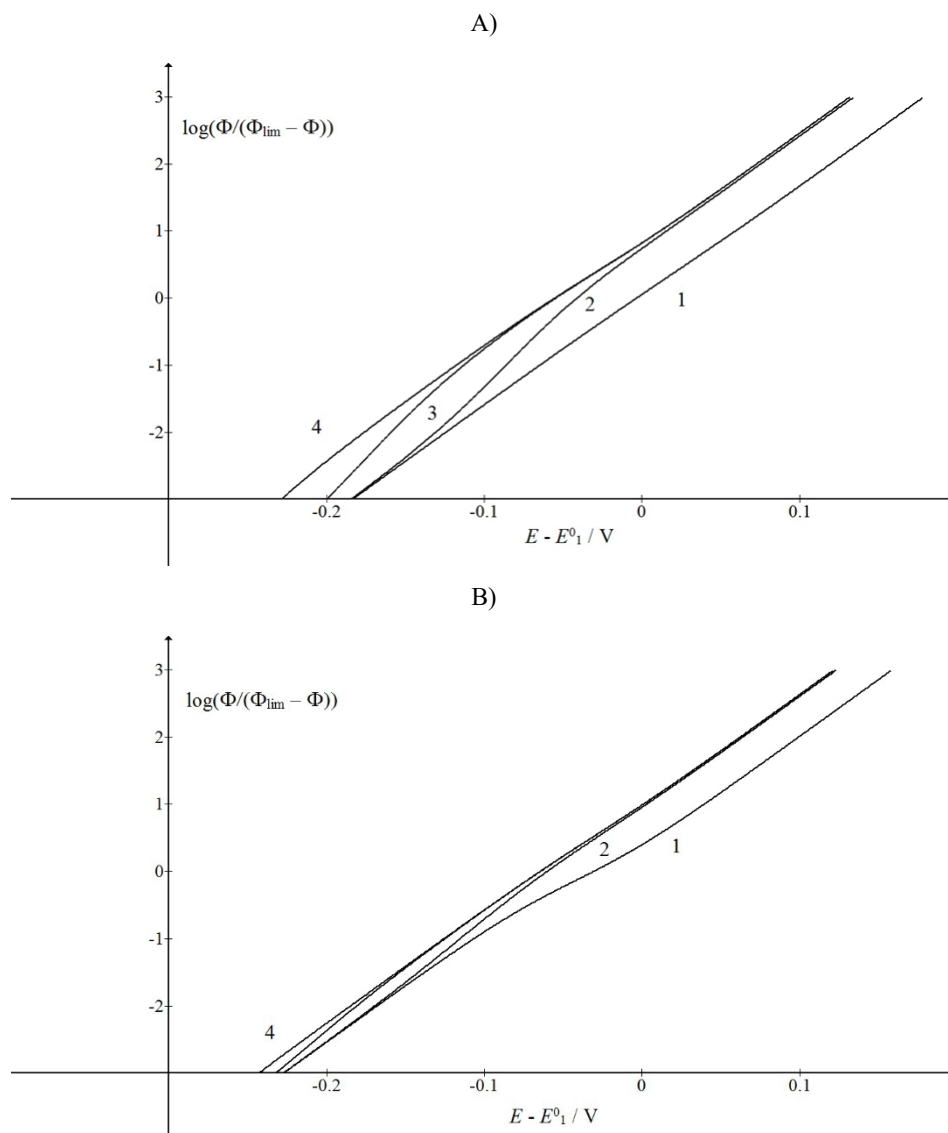

Fig. 5. Influence of the second standard potential on the logarithmic analyses of the ECE responses at high rotation rate. $Kc_A^* = 1$ (A) and 10^3 (B), $\omega = 40\pi$ rad/s and $(E_2^0 - E_1^0) / V = 0$ (1), –0.1 (2), –0.2 (3) and –0.3 (4). All other parameters are as in Fig. 2.

Fig. 6 shows the dependence of the dimensionless limiting currents of the waves on the logarithm of the product of the forward rate constant and the bulk concentration of the compound Y. This product can be achieved either by the variation of the product $k_f c_A^*$, keeping the ratio $c_Y^* / c_A^* = 1$, or by the variation of the ratio c_Y^* / c_A^*, keeping the product $k_f c_A^* = 1$ s^{-1}. Note that $\log(k_f c_Y^*) =$
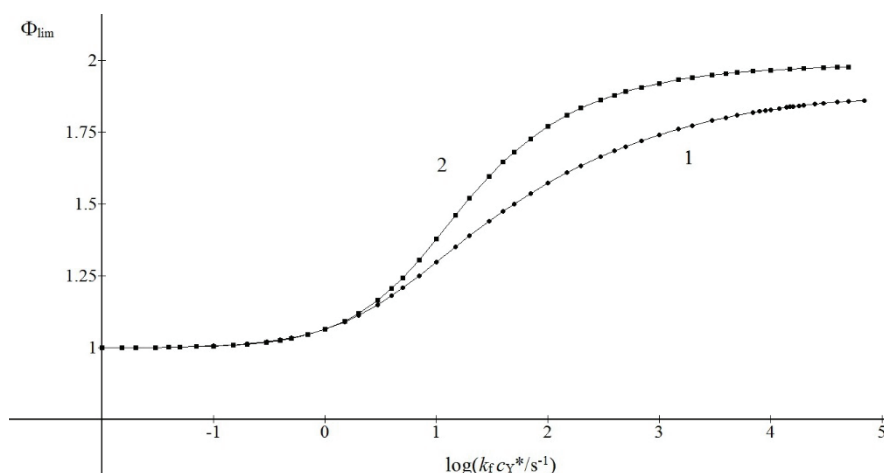
Fig. 6. Relationship between limiting currents of the ECE responses and the logarithm of the product $k_f c_Y^*$. $E_2^0 = E_1^0$, $Kc_A^* = 1$, $\omega = 40\pi$ rad/s and $c_Y^* = c_A^*$ (1) and $k_f c_A^* = 1$ s⁻¹ (2). All other parameters are as in Fig. 1.

$\log(k_f c_A^*)$ + $\log(c_Y^*/c_A^*)$. The results of these two procedures are not equal because of the diffusion of Y. Experimentally, these procedures can be performed if the concentrations of A and Y can be changed independently. If the bulk concentration of Y is fixed, then the product $k_f c_Y^*$ is also fixed and the kinetics of the ECE mechanism can be changed only by the variation of the rotation rate of electrode. In this research it is assumed that the concentration of Y can be changed. The basic difference between compounds A and Y is that the currents of both electrode reactions depend on the concentration of the first reactant A, but not on the concentration of compound Y. The latter is determining the forward rate of chemical reaction only. If the ratio c_Y^*/c_A^* is low, the chemical reaction consumes Y, regardless of the bulk concentration of A. The higher is c_A^*, the higher are currents and more Y is consumed. The change of Y concentration can be neglected only if the ratio c_Y^*/c_A^* is very high. Fig. 6 shows that for $c_Y^* = c_A^*$ the variation of reactant A concentration causes the increasing of limiting current to $\Phi_{lim} = 1.50$ if $k_f c_Y^* = 50$ s⁻¹ and that this current increases to 1.86 if $k_f c_Y^* = 6\times10^4$ s⁻¹. For $k_f c_A^* = 1$ s⁻¹ the variation of Y concentration results in $\Phi_{lim} = 1.52$ if $k_f c_A^* = 20$ s⁻¹ and $\Phi_{lim} = 1.98$ if $k_f c_Y^* = 5\times10^4$ s⁻¹. Fig. 7 shows that the ratio of concentrations of Y and A influences the form of the ECE responses. The corresponding half-wave potentials are shown in Fig. 8. If $c_Y^* = c_A^*$ the wave looks like a single electron polarogram and its $E_{1/2}$ changes from –4 to –1 mV. If $c_Y^*/c_A^* = 5\times10^4$ and $k_f c_A^* = 1$ s⁻¹, the response consists of two poorly separated waves and the half-wave potential is –0.054 V *vs.* E_1^0. Within the interval $1 < \log(k_f c_Y^*) < 3$ there is a linear relationship:

$$E_{1/2} - E_1^0 = -0.016\log(k_{\mathrm{f}} c_{\mathrm{Y}}^{*}) + 0.012 \text{ V} \qquad (22)$$
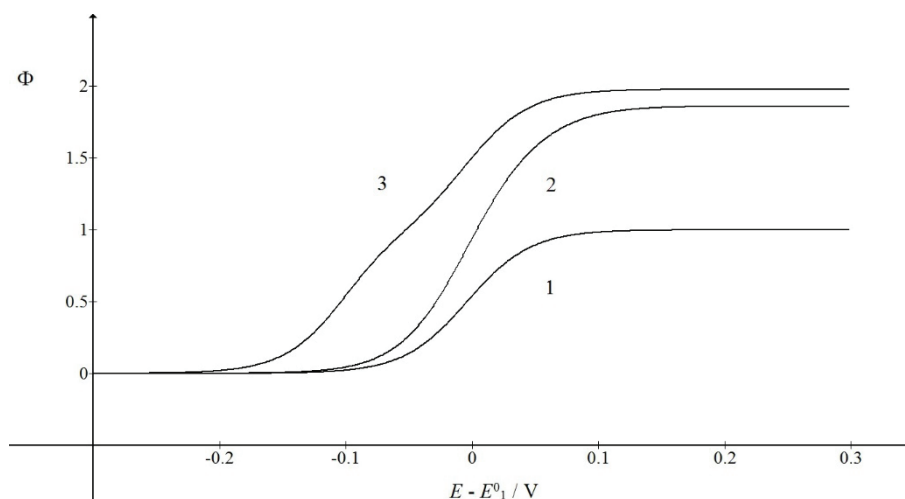

Fig. 7. Polarograms of the ECE mechanism; $k_{\mathrm{f}} c_{\mathrm{A}}^{*}$ / s^{-1} = 0 (1), 6×10^4 (2) and 1 (3) and $c_{\mathrm{Y}}^{*} / c_{\mathrm{A}}^{*}$ = 0 (1), 1 (2) and 5×10^4 (3). All other parameters are as in Fig. 6.
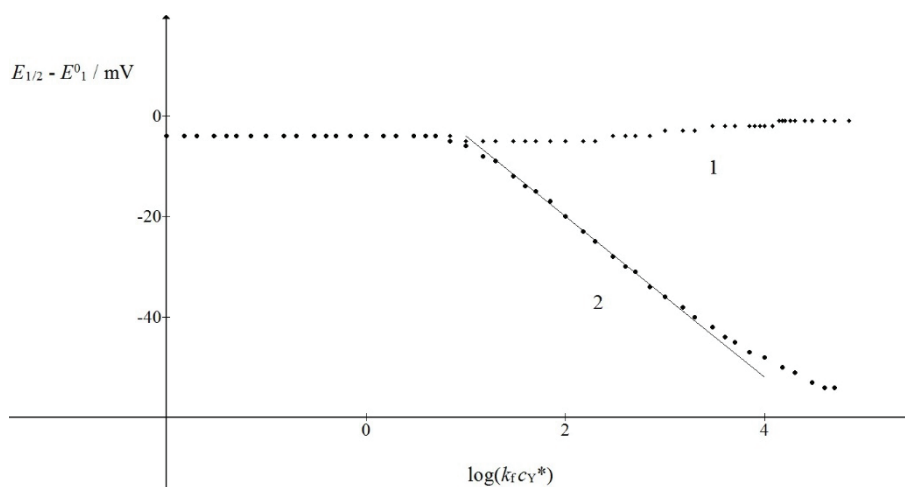
Fig. 8. Half-wave potentials of the ECE mechanism with reversible chemical reaction; $c_{\mathrm{Y}}^{*} = c_{\mathrm{A}}^{*}$ (1) and $k_{\mathrm{f}} c_{\mathrm{A}}^{*}$ = 1 s^{-1} (2). The straight line is defined by Eq. (22). All other parameters are as in Fig. 6.

The bulk concentration of Y influences only the forward rate of the chemical reaction, making the latter irreversible. This could mean that the responses corresponding to high values of the dimensionless equilibrium constant do not depend on the concentration of the compound Y. In Fig. 9 it is shown that this hypothesis is not true. The limiting currents are marked by 1 in Fig. 9A and were cal-
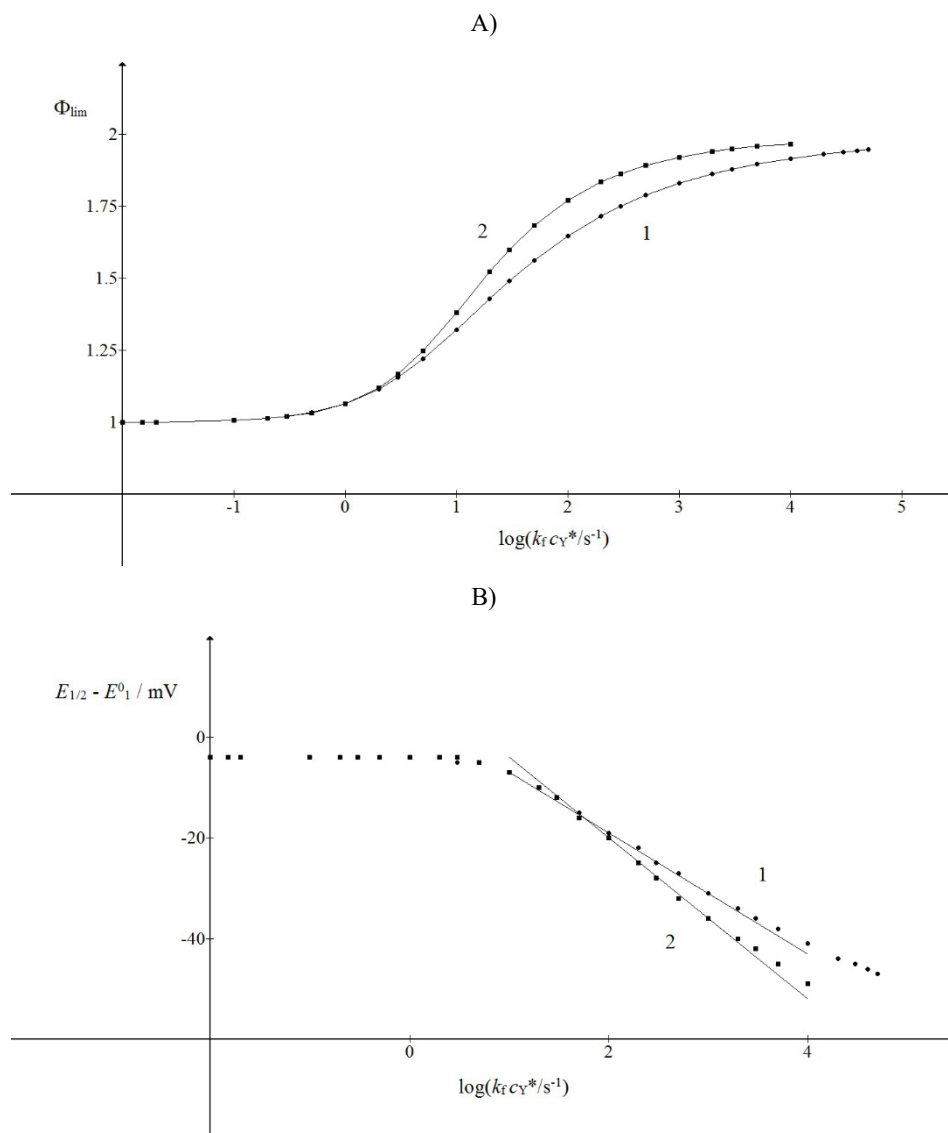
A)

B)

Fig. 9. The dependence of limiting currents (A) and half-wave potentials (B) of the ECE responses on the logarithm of the product $k_f c_Y^*$. $K c_A^* = 10^3$ and $c_Y^* = c_A^*$ (1) and $k_f c_A^* = 1$ s^{-1} (2). The straight lines 1 and 2 are defined by Eqs. (23) and (22), respectively. All other parameters are as in Fig. 6.

ulated by the variation of the product $k_f c_A^*$, assuming that $K c_A^* = 10^3$ and $c_Y^* / c_A^* = 1$. The same results were obtained for $K c_A^* = 10^4$, which means that the responses in Fig. 9 correspond to totally the irreversible chemical reaction. These kinetic currents are characterized by $\Phi_{lim} = 1.56$ if $k_f c_Y^* = 50$ s^{-1} and $\Phi_{lim} = 1.95$

if $k_f c_Y^* = 5\times10^4$ s^{-1}. These values are higher than those shown by curve 1 in Fig. 6, but they are lower than the limiting currents calculated by the variation of c_Y^* / c_A^* ratio keeping $k_f c_A^* = 1$ s^{-1} and $K c_A^* = 10^3$. These currents are shown by curve 2 in Fig. 9A. They are marked by $\Phi_{lim} = 1.52$ if $k_f c_Y^* = 20$ s^{-1} and $\Phi_{lim} = 1.97$ if $k_f c_Y^* = 10^4$ s^{-1}. These values are identical to the curve 2 in Fig. 6. So, again, it can be concluded that the effect of chemical reaction is the highest if the diffusion of compound Y can be neglected, and the chemical reaction is totally irreversible. In the simulation these conditions can be fulfilled if $c_Y = c_Y^*$ and $k_b = 0$. The results of such simulation are reported in Table II, and compared with the curve 2 in Fig. 9A. A small difference can be seen within the interval $1 < k_f c_Y^* < 100$. This means that the assumption $c_Y = c_Y^*$ is justified if $c_Y^* / c_A^* > 100$. The half-wave potentials of the irreversible ECE mechanisms are shown in Fig. 9B. They can be approximated by the straight lines in the interval $1 < \log(k_f c_Y^*) < 3$. The line 1 in Fig. 9B is defined by the following equation:

$$E_{1/2} - E_1^0 = -0.012\log(k_f c_Y^*) + 0.005 \text{ V} \tag{23}$$

The line 2 in this figure is defined by Eq. (22).

TABLE II. Limiting currents of the ECE waves influenced by the first order and the second order chemical reactions

$\log(k_f c_Y^*)$	$\Phi_{lim}(c_Y = c_Y^*)$	Φ_{lim} (Fig. 9A)
0	1.068	1.064
0.3	1.126	1.120
0.48	1.175	1.168
0.7	1.255	1.247
1	1.388	1.381
1.3	1.527	1.523
1.48	1.602	1.599
1.7	1.684	1.682
2	1.771	1.771

CONCLUSIONS

The ECE mechanism which consists of the two electrochemically reversible electrode reactions that are linked by a chemical reaction of the primary product B and the compound Y depends on the stability of the intermediate G. If the two waves appear, the limiting current of the second one depends on the kinetics of chemical reaction, and the rate constant can be estimated under certain conditions.[37] In this paper the two electro-oxidations with equal standard potentials were investigated. It is shown that the response is a single wave and that the limiting current depends on the kinetics of chemical reaction and its stability constant. The mechanism appears irreversible if the second standard potential is lower than the first one and also if the stability constant is high and the concen-

tration of the compound Y is much higher than the concentration of the initial reactant. The second order reaction depends on the diffusion of Y, but this can be neglected at very high concentrations and the reaction becomes to be the first order and totally irreversible. Under these conditions the mechanism is independent of the stability constant.

ИЗВОД

МОДЕЛОВАЊЕ ВОЛТАМЕТРИЈЕ СА ПРАВОУГАОНИМ ТАЛАСИМА ЗА ДВОЕЛЕКТРОНСКУ ИЗМЕНУ СПРЕГНУТУ СА ХЕМИЈСКОМ РЕАКЦИЈОМ НА РОТИРАЈУЋОЈ ДИСК ЕЛЕКТРОДИ

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Електрохемијска реакција двоелектронске измене спрегнута са хемијском реакцијом се назива ECE механизам. У овом истраживању је развијен модел волтаметрије са правоугаоним таласима на ротирајућој диск електроди, који укључује нестабилан интермедијар. Претпостављено је да су оба електрохемијска ступња брза и реверзибилна и да је хемијски ступањ реверзибилна реакција другог реда. Испитиван је утицај концентрације електрохемијски неактивне компоненте у хемијском ступњу и одређени су услови под којима тај ступањ постаје иреверзибилан и првог реда.

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