

Full Paper

Theory of Square-wave Voltammetry of two Electrode Reactions Coupled by Reversible Chemical Reaction

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Abstract- An ECE mechanism in which chemical reaction is permanently in equilibrium is investigated theoretically. The calculations were performed by the method of numerical integration for fast and reversible electrode reactions as well as for the reactions that are controlled by the electron transfer kinetics. In square-wave voltammetry the response depends on the difference in standard potentials of individual electron transfers and on the dimensionless equilibrium constant of the chemical reaction. Depending on the concentration of compound X⁻, which is one of reactants in chemical reaction, either a single peak or the split response may appear. In the first case the peak potential depends linearly on the logarithm of X⁻ concentration, with the slope $-2.3RT/2F$. The potential of the first peak of the split response is also linear function of, but the slope is $-2.3RT/F$. The relationship is determined between standard potentials and the critical value of the equilibrium constant above which the response splits in two peaks. Under the influence of electrode kinetics, the responses change with square-wave frequency. The first electron transfer is slow and the second one is fast if two peaks appear at the lowest frequency and merge into a single peak at the highest frequency. If the second charge transfer is slower than the first one, the difference in peak potentials increases with the increasing frequency.

Keyword- Reversible ECE Mechanism, Square-wave Voltammetry, Theory, Kinetics of Electrode Reactions

1. INTRODUCTION

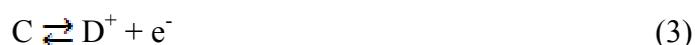
Two electrode reactions are coupled by a chemical reaction if the product of the first electrode reaction is the reactant of chemical reaction and the product of the latter is a reactant of the second electrode reaction [1-6]. This mechanism is marked by the acronym ECE. It was observed in the electroreductions of *p*-nitrosophenol [7], carbonylmanganese compounds [8], benzenesulfonyl fluoride [9], 1,4-benzenedisulfonyl difluoride [10], 1-butyl-3-methylimidazolium bistriflimide [11] and uranium complexes of acetylacetonate [12] as well as in the electrooxidations of carbonylmanganese complexes [13,14], tocopherols [15] and copper(II) complex of thyrotropin-releasing hormone [16]. There are several special cases of this mechanism, such as the chemical reaction of intermediate of the two-step electrode reaction [17,18], the disproportionation of the intermediate of two-step reaction [19] or the comproportionation of the reactant and the final product of the two-step reaction [20-23]. Also, the surface ECE mechanism that appears in electrochemistry of immobilized proteins was analyzed [24,25]. The theory of the ECE mechanism is developed for reversible electrode reactions coupled by either reversible [26-28] or totally irreversible chemical reactions [4,29,30]. The influences of the rate of chemical reaction and the difference in standard potentials of electrode reactions on the responses in *d.c.* polarography [26], chronoamperometry [27], cyclic voltammetry [4], rotating disk measurements [29] and square-wave voltammetry [28,30] are considered. In this communication the theory is extended to the kinetically controlled electrode reactions that are connected by the reversible chemical reaction.

2. EXPERIMENTAL

A Hewlett-Packard personal computer with an Intel Core 2 processor (3.1 GHz) and 6 GB memory was used. The calculations were performed with the Microsoft Quick Basic program. The double precision and 3×8150 reservations were used. The graphics were prepared with the program Sigma Plot 9.

2. 1.The model

The following reactions are investigated:



It is assumed that the mass transport can be described by the stationary, planar, semiinfinite diffusion model and that the compound X^- is present in great excess, so that the variation of its concentration can be neglected:

$$\frac{\partial c_A}{\partial t} = D \frac{\partial^2 c_A}{\partial x^2} \quad (4)$$

$$\frac{\partial c_P}{\partial t} = D \frac{\partial^2 c_P}{\partial x^2} \quad (5)$$

$$\frac{\partial c_{D^+}}{\partial t} = D \frac{\partial^2 c_{D^+}}{\partial x^2} \quad (6)$$

Here $c_P = c_{B^+} + c_C$ and the meanings of all other symbols are reported in Table 1. The initial and boundary conditions are as follows:

$$t = 0, x \geq 0: \quad c_A = c_A^*, \quad c_P = 0, \quad c_{D^+} = 0 \quad (7)$$

$$t > 0, x \rightarrow \infty: \quad c_A \rightarrow c_A^*, \quad c_P \rightarrow 0, \quad c_{D^+} \rightarrow 0 \quad (8)$$

$$x \geq 0: \quad c_{B^+} = c_P(1 + K_1)^{-1} \quad (9)$$

$$c_C = K_1 c_P(1 + K_1)^{-1} \quad (10)$$

$$K_1 = K c_{X^-} \quad (11)$$

$$K = c_C c_{B^+}^{-1} c_{X^-}^{-1} \quad (12)$$

$$x = 0: \quad \frac{I_1}{FS} = -k_{s1} \exp(-\alpha_1 \varphi_1) [(c_{B^+})_{x=0} - \exp(\varphi_1)(c_A)_{x=0}] \quad (13)$$

$$\varphi_1 = \frac{F}{RT} (E - E_{B/A}^0) \quad (14)$$

$$\frac{I_2}{FS} = -k_{s2} \exp(-\alpha_2 \varphi_2) [(c_{D^+})_{x=0} - \exp(\varphi_2)(c_C)_{x=0}] \quad (15)$$

$$\varphi_2 = \frac{F}{RT} (E - E_{D/C}^0) \quad (16)$$

$$D \left(\frac{\partial c_A}{\partial x} \right)_{x=0} = \frac{I_1}{FS} \quad (17)$$

$$D \left(\frac{\partial c_P}{\partial x} \right)_{x=0} = -\frac{I_1}{FS} + \frac{I_2}{FS} \quad (18)$$

$$D \left(\frac{\partial c_{D^+}}{\partial x} \right)_{x=0} = -\frac{I_2}{FS} \quad (19)$$

If electrode reactions (1) and (3) are fast and reversible, the conditions (13) and (15) can be replaced by Nernst equations:

$$(c_P)_{x=0} = (1 + K_1) \exp(\varphi_1) (c_A)_{x=0} \quad (20)$$

$$(c_{D^+})_{x=0} = K_1(1 + K_1)^{-1} \exp(\varphi_2) (c_P)_{x=0} \quad (21)$$

Equations (4)–(6) are converted into integral equations by Laplace transformations and solved by the numerical integration [3,31]. The solution is a system of recursive formulae for the dimensionless current $\Phi = I(FSc_A^*)^{-1}(Df)^{-1/2}$:

$$\Phi_{2,1} = RN^{-1}Q^{-1} \quad (22)$$

$$\Phi_{1,1} = MK_1^{-1} \exp(-\varphi_2) \Phi_{2,1} \quad (23)$$

$$\Phi_{2,m} = RN^{-1}Q^{-1} + (N^{-1} - ZK_1^{-1} \exp(-\varphi_2))Q^{-1} \sum_{j=1}^{m-1} \Phi_{2,j} S_{m-j+1} + (1 - VN^{-1})Q^{-1} \sum_{j=1}^{m-1} \Phi_{1,j} S_{m-j+1} \quad (24)$$

$$\Phi_{1,m} = RN^{-1} - VN^{-1} \sum_{j=1}^{m-1} \Phi_{1,j} S_{m-j+1} + N^{-1}(\Phi_{2,m} + \sum_{j=1}^{m-1} \Phi_{2,j} S_{m-j+1}) \quad (25)$$

$$M = 5\sqrt{\pi/2} \lambda_2^{-1} \exp(\alpha_2 \varphi_2) (1 + K_1) + Z \quad (26)$$

$$N = 5\sqrt{\pi/2} \lambda_1^{-1} \exp(\alpha_1 \varphi_1) (1 + K_1) + V \quad (27)$$

$$Q = MK_1^{-1} \exp(-\varphi_2) - N^{-1} \quad (28)$$

$$R = (1 + K_1) \exp(\varphi_1) 5\sqrt{\pi/2} \quad (29)$$

$$Z = 1 + K_1 + K_1 \exp(\varphi_2) \quad (30)$$

$$V = 1 + (1 + K_1) \exp(\varphi_1) \quad (31)$$

$$\lambda_1 = k_{s1} (Df)^{-1/2} \quad (32)$$

$$\lambda_2 = k_{s2} (Df)^{-1/2} \quad (33)$$

$$S_k = \sqrt{k} - \sqrt{k-1} \quad (34)$$

If both electrode reactions are fast and reversible the following solution is obtained:

$$\Phi_{2,1} = RV^{-1} (1 + (1 + K_1) K_1^{-1} \exp(-\varphi_2) - V^{-1})^{-1} \quad (35)$$

$$\Phi_{1,1} = RV^{-1} + V^{-1} \Phi_{2,1} \quad (36)$$

$$\Phi_{2,m} = RV^{-1} (1 + (1 + K_1) K_1^{-1} \exp(-\varphi_2) - V^{-1})^{-1} - \sum_{j=1}^{m-1} \Phi_{2,j} S_{m-j+1} \quad (37)$$

$$\Phi_{1,m} = RV^{-1} - \sum_{j=1}^{m-1} \Phi_{1,j} S_{m-j+1} + V^{-1} (\Phi_{2,m} + \sum_{j=1}^{m-1} \Phi_{2,j} S_{m-j+1}) \quad (38)$$

$$2 \leq m \leq W \quad (39)$$

$$W = 50(E_{start} - E_{final})/dE \quad (40)$$

A sum of currents $\Phi_m = \Phi_{1,m} + \Phi_{2,m}$ is calculated as a function of potential for the excitation signal of square-wave voltammetry. Each square-wave half-period is divided into 25 time increments. In all calculations the square-wave amplitude $E_{sw}=50$ mV and the potential step increment $dE=5$ mV were used.

3. RESULTS AND DISCUSSION

If both electrode reactions (1) and (3) are fast and reversible, square-wave voltammograms of the ECE mechanism depend on the difference in standard potentials $E_{B/A}^0$ and $E_{D/C}^0$ and on the dimensionless constant K_1 , which is the product of the equilibrium constant of chemical reaction (2) and the concentration of compound X^- . For equal standard potentials the responses are split in two peaks if either $K_1 > 100$ or $K_1 < 0.01$. This is shown in Fig. 1. These examples are not representations of some particular electrode reactions, but they are generalization of ECE mechanisms of benzophenone [11] and tocopherol [15]. These voltammograms correspond to three groups of reactions. The calculations are performed under the assumption that the compound X^- is present in great excess. So, the variations of the product K_1 can be achieved either by changing the concentration of X^- , or by assuming different stability constants K .

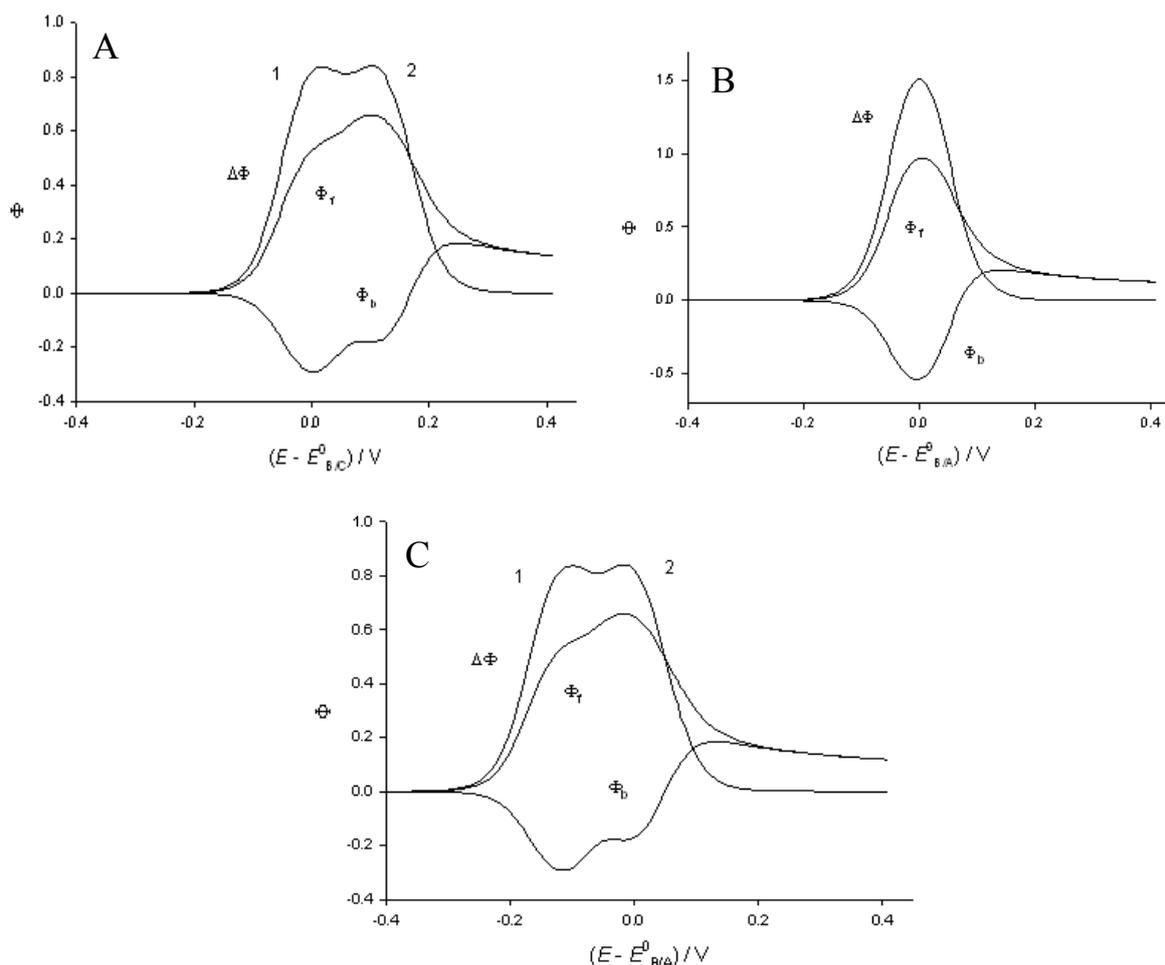


Fig. 1 Theoretical square-wave voltammograms (SWV) of reversible ECE mechanism. $E_{D/C}^0 = E_{B/A}^0$, $E_{SW} = 50$ mV, $dE = 5$ mV and $K_1 = 0.01$ (A), 1 (B) and 100 (C). Dimensionless net currents ($\Delta\Phi$) and their forward (Φ_f) and backward (Φ_b) components are shown. The first and the second peak of the split response are marked

Table 1. Meanings of symbols

α_1, α_2	Transfer coefficients of the first and the second electron transfer steps
c_A, c_P, c_D	Concentrations of the reactant, intermediate and product
c_A^*	Concentration of the reactant in the bulk of solution
D	Common diffusion coefficient
dE	Square-wave potential increment
E	Electrode potential
$E_{B/A}^0, E_{D/C}^0$	Standard potentials of the first and the second electron transfer steps
E_{sw}	Square-wave amplitude
E_{st}	Square-wave starting potential
E_p	Peak potential
$E_{p,f}, E_{p,b}$	Peak potentials of the forward and backward components
F	Faraday constant
f	Square-wave frequency
Φ	Dimensionless current
$\Delta\Phi_p$	Dimensionless net peak current
Φ_f, Φ_b	Dimensionless forward and backward currents
$\Phi_{p,f}, \Phi_{p,b}$	Dimensionless forward and backward peak currents
I_1, I_2	Currents of the first and the second electron transfers
k_{s1}, k_{s2}	Standard rate constants of the first and the second electron transfer steps
λ_1, λ_2	Dimensionless kinetic parameters of the first and the second electron transfers
R	Gas constant
S	Electrode surface area
t	Time
x	Distance perpendicular to the electrode surface

In the experiments the concentration of the reactant A can be 10^{-5} mol/L, which means that the concentration of the compound X⁻ must be equal or higher than 10^{-3} mol/L. If the latter is varied within the interval $1 \geq c_{X^-}/(\text{mol/L}) \geq 10^{-3}$ and K is either 10^3 L/mol, or 1 L/mol, the variation of dimensionless constant is $10^3 \geq K_1 \geq 1$ in the first case and $1 \geq K_1 \geq 10^{-3}$ in the second one. Also, the conditions $10 \geq K_1 \geq 0.1$ correspond to the combination of $1 \geq c_{X^-}/(\text{mol/L}) \geq 10^{-2}$ with $K=10$ L/mol. This is physical meaning of the results shown in Fig. 2, in which the dependence of dimensionless peak currents and peak potentials on the logarithm of the constant K_1 is reported. These results can be better understood if two limiting cases of ECE mechanism are firstly considered. The first case is a simple one electron reaction that corresponds to $K_1 = 0$. For $E_{sw} = 50$ mV and $dE = 5$ mV,

the dimensionless net peak current and net peak potential are $\Delta\Phi_p = 0.7520$ and $E_p = E_{B/A}^0$. The extremes of the forward and backward components are $\Phi_{p,f} = 0.4836$, $E_{p,f} - E_{B/A}^0 = 0.005$ V, $\Phi_{p,b} = -0.2707$ and $E_{p,b} - E_{B/A}^0 = -0.005$ V. If the intermediate is stable ($E_{D/C}^0 - E_{B/A}^0 \geq 0.3$ V) and $K_1 \neq 0$ the response consists of two well separated peaks that correspond to one electron transfer each. For instance, if $K_1 = 100$ and $E_{D/C}^0 - E_{B/A}^0 = 0.3$ V, the net peak currents are $\Delta\Phi_{p,1} = 0.7517$ and $\Delta\Phi_{p,2} = 0.7522$, and net peak potentials are $E_{p,1} = -0.120$ V vs. $E_{B/A}^0$ and $E_{p,2} = E_{D/C}^0$. The second limiting case appears if the intermediate is highly unstable ($E_{D/C}^0 \ll E_{B/A}^0$) and $K_1 \neq 0$, so that the ECE mechanism can be described by the two electron electrode reaction: $A + X^- \rightleftharpoons D^+ + 2e^-$. For the same signal parameters E_{sw} and dE , the response of this reaction is a single peak with the maximum $\Delta\Phi_p = 1.9115$ that appears at $E_p = E_{D/A}^0$. The standard potential $E_{D/A}^0$ depends on the logarithm of the dimensionless equilibrium constant: $E_{D/A}^0 = -(RT/2F)\ln K_1 + (E_{B/A}^0 + E_{D/C}^0)/2$. An example of this limiting case appears if $E_{D/C}^0 - E_{B/A}^0 = -0.3$ V and $K_1 = 100$. Under these conditions the net peak current and peak potential are $\Delta\Phi_p = 1.9038$ and $E_p = -0.210$ V vs. $E_{B/A}^0$. The latter is equal to $E_{D/A}^0$.

If $K_1 > 100$ and $E_{D/C}^0 = E_{B/A}^0$, the separation between the first and the second peak depends linearly on the logarithm of K_1 . This is shown on the right hand side of Fig. 2. The slope of the straight line 2 is $\Delta E_{p,1}/\Delta \log K_1 = -2.3RT/F$. It is caused by the chemical reaction that consumes the immediate product B^+ of the first electrode reaction [18,28]. The potential of the second peak tends to $E_{D/C}^0$ as K_1 increases because the concentration of the second reactant C becomes independent of K_1 under this condition (see eq. 10). The peak currents $\Delta\Phi_{p,1}$ and $\Delta\Phi_{p,2}$ of these responses are equal and tend to 0.7520, which corresponds to one electron transfer. The left hand side of Fig. 2 is symmetrical with the right one. The first peak potential tends to $E_{B/A}^0$ because the concentration of product B^+ does not depend on K_1 (see eq. 9) and the second peak potential depends linearly on the logarithm of K_1 with the slope $\Delta E_{p,2}/\Delta \log K_1 = -2.3RT/F$ (see the straight line 3 in Fig. 2B). The latter is caused by the diminished concentration of C. Similar relationship between peak potential and the logarithm of ligand concentration appears in voltammetry of labile metal complexes [32,33]. The net peak currents of two peaks are equal and become independent of K_1 if it is smaller than 10^{-3} . Within the interval $-2 < \log K_1 < 2$ the response is a single peak (see Fig. 1B) with the maximum at $E_{D/A}^0$. For this reason the peak potential is linear function of the logarithm of K_1 , with the slope $\Delta E_p/\Delta \log K_1 = -2.3RT/2F$ (see the straight line 1 in Fig. 2B). The net peak current is the highest if $K_1 = 1$ and decreases if either $K_1 > 1$ or $K_1 < 1$. The maximum value $\Delta\Phi_p = 1.5041$ is smaller than 1.9115 because the condition $E_{D/C}^0 \ll E_{B/A}^0$ is not satisfied. The decreasing of $\Delta\Phi_p$ is caused by the gradual separation of two peaks. Before the two net peaks appear, the forward and backward components of the single peak start to separate. If $0.2 \leq K_1 \leq 5$ the difference between peak potentials of forward and backward components is 10 mV (see Fig. 1B). Outside this range the components are similar to those that are shown in

Figs. 1A and 1C. The forward component is in maximum at the potential that is higher than the net peak potential, while the potential of minimum of backward component is lower than the net peak potential. This is shown by crosses and diamonds for $1 \leq \log K_1 \leq 2$ and $-2 \leq \log K_1 \leq -1$ in Fig. 2.

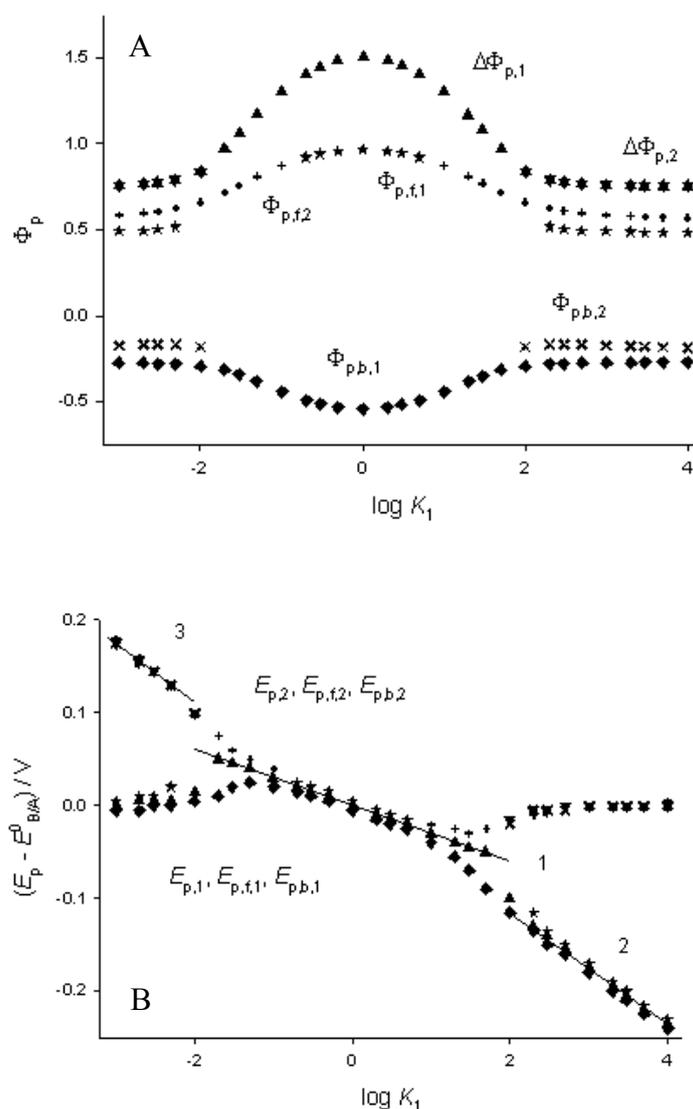


Fig. 2. SWV of reversible ECE mechanism. Dependence of dimensionless peak currents (A) and peak potentials (B) on the logarithm of dimensionless equilibrium constant of chemical reaction. $E_{D/C}^0 = E_{B/A}^0$, $E_{SW}=50$ mV, $dE=5$ mV, $\Delta\Phi_{p,1}, E_{p,1}$ (\blacktriangle), $\Phi_{p,f,1}, E_{p,f,1}$ (\star), $\Phi_{p,b,1}, E_{p,b,1}$ (\blacklozenge), $\Delta\Phi_{p,2}, E_{p,2}$ (\blacktriangledown), $\Phi_{p,f,2}, E_{p,f,2}$ (\oplus) and $\Phi_{p,b,2}, E_{p,b,2}$ (\times)

The influence of the difference in standard potentials on the net peak currents and net peak potentials is shown in Fig. 3. If $E_{D/C}^0 - E_{B/A}^0 = -0.1$ V the response is a single peak for $-4 < \log K_1 < 3.7$. The net peak current depends parabolically on the logarithm of dimensionless

constant K_1 , with the maximum $\Delta\Phi_p = 1.8403$ that appears for $K_1=1$ at $E_p = -0.050$ V vs. $E_{B/A}^0$, which is equal to $E_{D/A}^0$ for these conditions. The slope of the straight line (d) in Fig. 3B is $-2.3RT/2F$, which means that the net peak potential is equal to $E_{D/A}^0$ for all K_1 values for which the response is not split. If $\log K_1 \geq 3.7$ the second peak appears. Its net peak current is equal to the net peak current of the first peak and tends to 0.7520 as K_1 increases. The peak potential of the second peak is equal to -0.1 V vs. $E_{B/A}^0$ if $K_1 > 2 \times 10^4$ while the first peak potential is a linear function of $\log K_1$, with the slope $\Delta E_{p,1}/\Delta \log K_1 = -2.3RT/F$, which is shown by the straight line (c) in Fig. 3B.

The results marked by 2 in Fig. 3 are calculated for $E_{D/C}^0 - E_{B/A}^0 = 0.1$ V. These responses consist of two peaks for all K_1 values. The peak currents of these two peaks are equal and decrease from 0.7913, for $K_1 = 1$, to 0.7520 for either $K_1 > 10^3$ or $K_1 < 10^{-3}$. If $K_1 < 0.5$ the first peak potential is equal to $E_{B/A}^0$, while the second peak potential is a linear function of $\log K_1$, with the slope $\Delta E_{p,2}/\Delta \log K_1 = -2.3RT/F$ (see the straight line (a) in Fig. 3B). Furthermore, if $K_1 > 2$ the second peak potential is equal to $E_{D/C}^0$ and the first one depends on $\log K_1$, with the slope $\Delta E_{p,1}/\Delta \log K_1 = -2.3RT/F$ (the straight line (b) in Fig. 3B).

Comparing Figs. 2B and 3B one can notice that the value of dimensionless constant K_1 at which the response splits in two peaks depends on the difference in standard potentials. This relationship was investigated for $K_1 > 1$ within the interval $-0.120 \leq (E_{D/C}^0 - E_{B/A}^0) / \text{V} \leq 0.050$ and the following function was discovered: $\log(K_1)_{crit} = -17.035 \times (E_{D/C}^0 - E_{B/A}^0) + 1.863$. The slope is reported in V^{-1} . Below the critical value of K_1 a single peak appears.

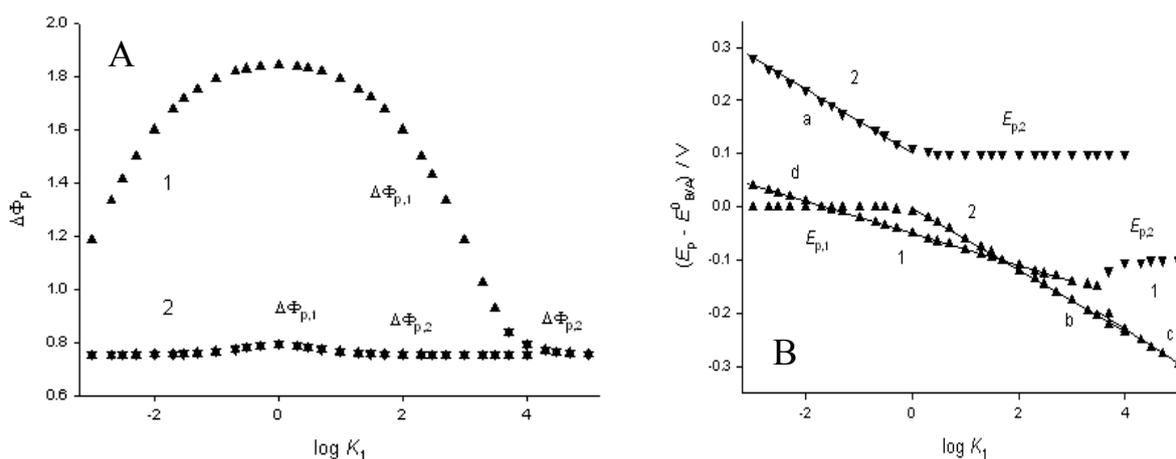


Fig. 3. SWV of reversible ECE mechanism. Dependence of dimensionless peak currents (A) and peak potentials (B) on the logarithm of dimensionless equilibrium constant of chemical reaction. $(E_{D/C}^0 - E_{B/A}^0) / \text{V} = -0.1$ (1) and 0.1 (2), $E_{\text{SW}} = 50$ mV, $dE = 5$ mV, $\Delta\Phi_{p,1}$, $E_{p,1}$ (\blacktriangle) and $\Delta\Phi_{p,2}$, $E_{p,2}$ (\blacktriangledown)

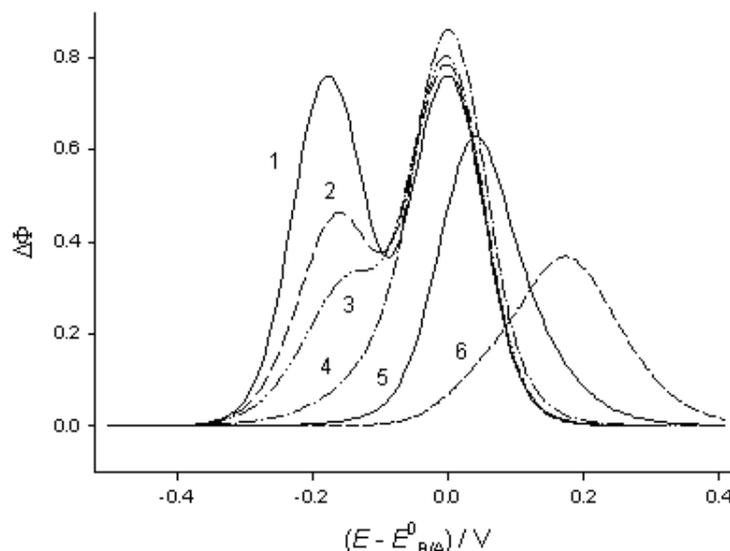


Fig. 4. Theoretical square-wave voltammograms of ECE mechanism influenced by the kinetics of the first electron transfer; $E_{D/C}^0 = E_{B/A}^0$, $\alpha_1=0.5$, $\alpha_2=0.5$, $K_1=1000$, $\lambda_2=1000$, $E_{SW} = 50$ mV, $dE=5$ mV and $\lambda_1=1000$ (1), 10 (2), 5 (3), 1 (4), 0.1 (5) and 0.01 (6)

Fig. 5 shows the details of these processes. The maxima of the first peak and its forward component disappear below $\lambda_1=10$, but the minimum of the backward component of the first peak can be determined down to $\lambda_1=0.5$. The second net peak current increases from 0.7604, for $\lambda_1=10^3$, to 0.8584, for $\lambda_1=1$, and decreases to 0.3630 for $\lambda_1=10^{-3}$. Below $\lambda_1=0.1$ the maximum of forward component is higher than the net peak current, which is an indication of irreversible process. This is confirmed by the disappearing of backward component below $\lambda_1=0.01$. Under this condition the second net peak potential depends linearly on the logarithm of the first kinetic parameter, with the slope $\Delta E_{p,2}/\Delta \log \lambda_1 = -2.3RT/(1 - \alpha_1)F$ (see the straight line (1) in Fig. 5B). Considering eq. (32) this means that this peak potential is a linear function of the logarithm of square-wave frequency, with the slope $\Delta E_{p,2}/\Delta \log f = 2.3RT/2(1 - \alpha_1)F$. In the range of λ_1 values in which the minimum of backward component of the first peak gradually vanishes there is a linear relationship between the potential of this minimum and $\log \lambda_1$, with the slope $2.3RT/\alpha_1 F$ (see the straight line (2) in Fig. 5B). These minima correspond to slow reduction of the intermediate B^+ . The potentials of minima of backward components of the second peak are equal 0.025 V vs. $E_{B/A}^0$ if $\lambda_1 \leq 0.01$. This is because the reduction of D^+ to C is reversible.

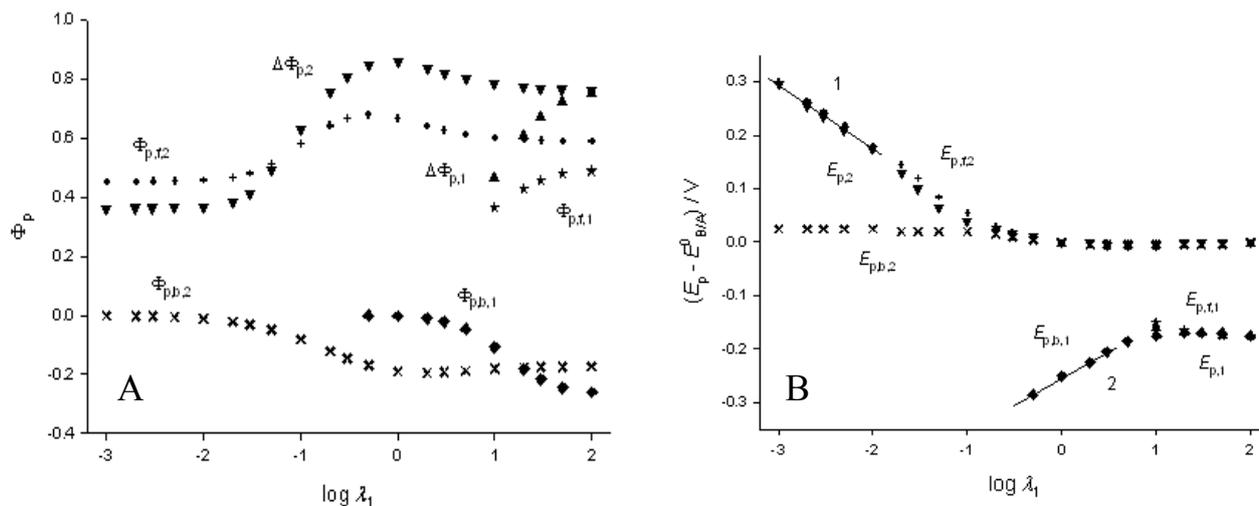


Fig. 5. SWV of ECE mechanism influenced by electrode kinetics. Dependence of dimensionless peak currents (A) and peak potentials (B) on the logarithm of dimensionless kinetic parameter of the first electron transfer. $E_{D/C}^0 = E_{B/A}^0$, $\alpha_1=0.5$, $\alpha_2=0.5$, $K_1=1000$, $\lambda_2=1000$, $E_{SW}=50$ mV, $dE=5$ mV, $\Delta\Phi_{p,1}$, $E_{p,1}$ (\blacktriangle), $\Phi_{p,f,1}$, $E_{p,f,1}$ (\star), $\Phi_{p,b,1}$, $E_{p,b,1}$ (\blacklozenge), $\Delta\Phi_{p,2}$, $E_{p,2}$ (\blacktriangledown), $\Phi_{p,f,2}$, $E_{p,f,2}$ (\oplus), and $\Phi_{p,b,2}$, $E_{p,b,2}$ (\times)

In the case that the first electron transfer is reversible and the second one is kinetically controlled, the separation between two peaks increases as the frequency is increased. This is shown in Figs. 6 and 7. If the response of reversible ECE mechanism is split in two peaks, the net peak current of the second peak is diminished from 0.7426 to 0.1832 within the interval $10 \geq \lambda_2 \geq 0.1$, while the first net peak current changes only from 0.8252 to 0.7541 within this interval. If $\lambda_2 < 0.1$ the net peak potential of the second peak and the logarithm of the second kinetic parameter are linearly related, with the slope $\Delta E_{p,2}/\Delta \log \lambda_2 = -2.3RT/(1 - \alpha_2)F$, while the first net peak potential is independent of λ_2 . The dimensionless constant K_1 influences the value of kinetic parameter λ_2 at which two separated peaks appear, or the separation between them start to increase. If $K_1=1$ and $E_{D/C}^0 = E_{B/A}^0$ the response of reversible ECE mechanism is a single peak that is shown in Fig. 1B. Within the interval $10 \geq \lambda_2 \geq 0.1$ the net peak current decreases from 1.5011 to 0.8251, but no second peak appear above $\lambda_2=0.03$. It happens when the second electron transfer is totally irreversible, which is confirmed by the linear relationship between $E_{p,2}$ and $\log \lambda_2$ below $\lambda_2=0.01$. The net peak currents of irreversible electron transfer do not depend on the constant K_1 .

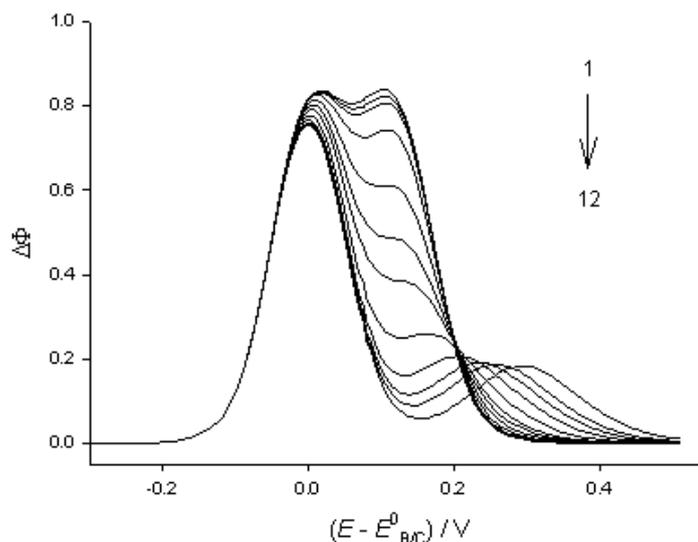


Fig. 6. Theoretical square-wave voltammograms of ECE mechanism influenced by the kinetics of the second electron transfer; $E_{D/C}^0 = E_{B/A}^0$, $\alpha_1=0.5$, $\alpha_2=0.5$, $K_1=0.01$, $\lambda_1=100$, $E_{SW}=50$ mV, $dE=5$ mV and $\lambda_2=100$ (1), 30 (2), 20 (3), 10 (4), 5 (5), 3 (6), 2 (7), 1 (8), 0.5 (9), 0.3 (10), 0.2 (11) and 0.1 (12)

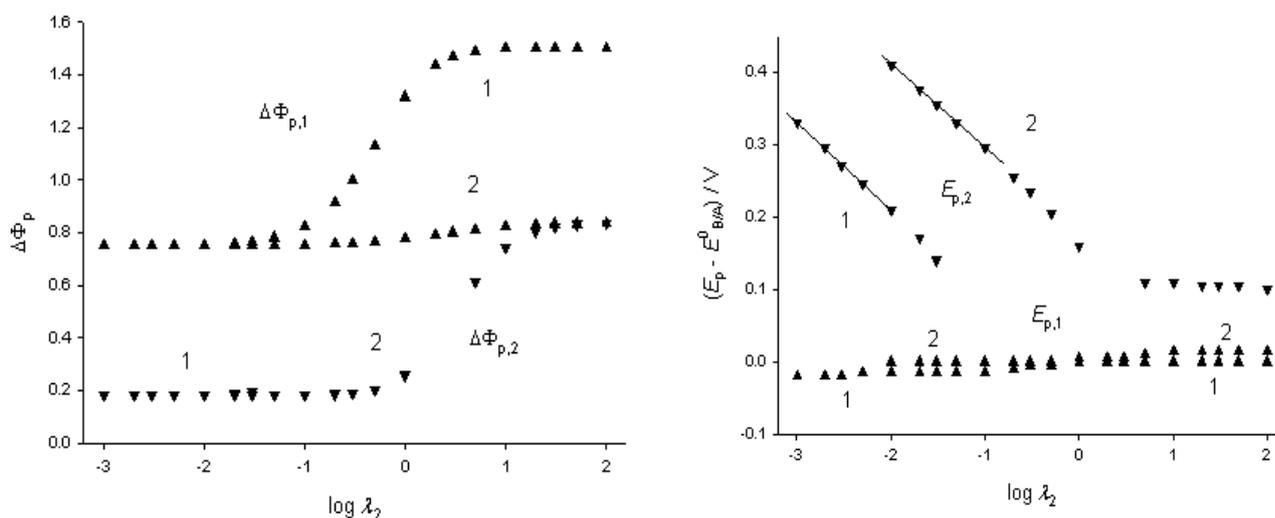


Fig. 7. SWV of ECE mechanism influenced by electrode kinetics. Dependence of dimensionless peak currents (A) and peak potentials (B) on the logarithm of dimensionless kinetic parameter of the second electron transfer; $E_{D/C}^0 = E_{B/A}^0$, $\alpha_1=0.5$, $\alpha_2=0.5$, $\lambda_1=100$, $E_{SW}=50$ mV, $dE=5$ mV, $\Delta\Phi_{p,1}$, $E_{p,1}$ (\blacktriangle) $\Delta\Phi_{p,2}$, $E_{p,2}$ (\blacktriangledown) and $K_1=1$ (1) and 0.01 (2)

4. CONCLUSION

Square-wave voltammograms of reversible ECE mechanism depend on the concentration of compound X⁻, the stability constant of chemical reaction and the difference in standard potentials of individual electron transfers. The peak currents are linearly proportional to the

square-root of frequency and peak potentials are independent of frequency. If a single peak appears for all concentrations of X^- , the net peak potential depends linearly on the logarithm of concentration of X^- , with the slope $-2.3RT/2F$, and the concentration of X^- satisfies the following relationship: $\log c_{X^-} < \log(K_1)_{crit} - \log K$. If two peaks appear and the net peak potential of the first one is linear function of $\log c_{X^-}$, with the slope $-2.3RT/F$, while the net peak potential of the second peak is independent of the concentration of X^- , this means that either $E_{D/C}^0 - E_{B/A}^0 > 0.050$ V and $K_1 > 1$, or $\log c_{X^-} > \log(K_1)_{crit} - \log K$. The responses of ECE mechanism in which one or both electrode reactions are kinetically controlled depend on square-wave frequency. If two peaks appear at the lowest frequency and merge into a single peak at the highest frequency, then the first electron transfer is slow and the second one is fast. The difference in peak potentials increases with the increasing frequency if the second charge transfer is slow.

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