Square-wave Voltammetry of Two-step Electrode Reaction

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A theory of square-wave voltammetry of two-step electrode reaction with kinetically controlled electron transfers is developed and a special case of thermodynamically unstable intermediate is analyzed. If the first electron transfer is slower than the second one, the transfer coefficients can be determined by the application of cathodic and anodic scan directions.

1. INTRODUCTION

Electrode reactions that consist of transfers of two electrons may occur through two consecutive steps [1 - 4]. Theory of this mechanism is developed for chronoamperometry [5 - 7], direct current [8 - 13], normal pulse [14] and differential pulse polarography [15, 16] and cyclic [17 - 22] and additive differential pulse voltammetry [23, 24]. If both charge transfers are fast and reversible, the response of simple two-electrons reaction depends only on thermodynamic stability of the intermediate [9]. For the reduction process, two peaks or waves appear if the standard potential of the second electron transfer is more than 100 mV lower than the standard potential of the first electron transfer [15, 19]. If this condition is not satisfied, a single peak or wave appears [11, 17]. In the case that charge transfers are kinetically controlled, the response depends on the standard rate constants and transfer coefficients of both steps [10, 14, 18, 22, 25]. In many cases the first step is slower than the second one and the intermediate is unstable [2]. Under these conditions the transfer coefficient of the first step can be determined [5, 14, 22, 26]. There are, however, electrode reactions in which the response is influenced by the kinetics of the second step as well [6, 25 - 31]. In this paper the theory of two subsequent quasireversible electron transfers is developed for the direct and reverse square-wave voltammetry. In the latter technique the scan starts at the potential at which the reactant is not stable at

the electrode surface [32, 33]. This model is used to investigate the relationship between the properties of the square-wave voltammogram and the kinetic parameters of electrode reaction.

2. THE MODEL

An electrode reaction that occurs through two consecutive steps is analyzed:

$$Ox^{(p+2)+} + e^- \rightleftharpoons Int^{(p+1)+} \tag{1}$$

$$Int^{(p+1)+} + e^- \rightleftharpoons Red^{p+} \tag{2}$$
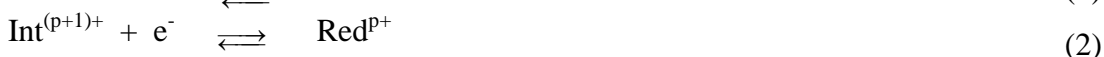
For the stationary, planar, semi-infinite diffusion, the following system of differential equations has to be solved:

$$\frac{\partial c_{Ox}}{\partial t} = D \frac{\partial^2 c_{Ox}}{\partial x^2} \tag{3}$$

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

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

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

$$t > 0, x \to \infty: c_{Ox} \to c_{Ox}^*, c_{Int} \to 0, c_{Red} \to 0 \tag{7}$$

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

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

$$D \left(\frac{\partial c_{Red}}{\partial x}\right)_{x=0} = \frac{I_2}{FS} \tag{10}$$

$$\frac{I_1}{FS} = -k_{s,1} exp(-\alpha_1 \varphi_1)[(c_{Ox})_{x=0} - (c_{Int})_{x=0} exp(\varphi_1)] \tag{11}$$

$$\frac{I_2}{FS} = -k_{s,2} exp(-\alpha_2 \varphi_2)[(c_{Int})_{x=0} - (c_{Red})_{x=0} exp(\varphi_2)] \tag{12}$$

$$\varphi_1 = \frac{F}{RT}(E - E_1^0) \tag{13}$$

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

The meanings of all symbols are reported in the Table 1. Differential equations (3) – (5) are solved by Laplace transformations and by the method of numerical integration proposed by Olmstead and Nicholson [34]. The solution is the system of recursive formulae for the dimensionless current $\Phi_i = I_i(FSc_{Ox}^*)^{-1}(Df)^{-1/2}$, where $i = 1$ or 2. The sum $\Phi = \Phi_1 + \Phi_2$ is reported as a function of electrode potential.

$$\Phi_{1,m} = Z_m \left[\frac{-5\sqrt{\pi}}{exp(\varphi_{1,m})\sqrt{2}} + V_m \sum_{j=1}^{m-1} \Phi_{1,j} S_{m-j+1} + W_m \sum_{j=1}^{m-1} \Phi_{2,j} S_{m-j+1} \right] \tag{15}$$

$$\Phi_{2,m} = \Phi_{1,m} \left[\frac{5\sqrt{\pi} exp(-(1-\alpha_1)\varphi_{1,m})}{\lambda_1\sqrt{2}} + \left(1 + exp(-\varphi_{1,m})\right) \right] + \frac{5\sqrt{\pi}}{exp(\varphi_{1,m})\sqrt{2}} +$$

$$\left(1 + exp(\varphi_{1,m})\right) exp(-\varphi_{1,m}) \sum_{j=1}^{m-1} \Phi_{1,j} S_{m-j+1} - \sum_{j=1}^{m-1} \Phi_{2,j} S_{m-j+1} \tag{16}$$

$$Z_m = N_m^{-1} \lambda_1 exp\left((1-\alpha_1)\varphi_{1,m}\right) \sqrt{2} \left[5\sqrt{\pi} + \lambda_2 exp(-\alpha_2\varphi_{2,m})\left(1 + exp(\varphi_{2,m})\right)\sqrt{2}\right] \tag{17}$$

$$N_m =$$

$$\left[5\sqrt{\pi} + \lambda_1 exp(-\alpha_1\varphi_{1,m})\left(1 + exp(\varphi_{1,m})\right)\sqrt{2}\right]\left[5\sqrt{\pi} + \lambda_2 exp(-\alpha_2\varphi_{2,m})\left(1 + exp(\varphi_{2,m})\right)\sqrt{2}\right] -$$

$$2\lambda_1\lambda_2 exp\left((1-\alpha_1)\varphi_{1,m}\right) exp(-\alpha_2\varphi_{2,m})$$

$$\tag{18}$$

$$V_m = \left[-\left(1 + exp(\varphi_{1,m})\right) 5\sqrt{\pi} - \lambda_2 \sqrt{2} exp(-\alpha_2 \varphi_{2,m}) - \lambda_2 \sqrt{2} \left(1 + exp(\varphi_{1,m})\right) exp\left((1 - \alpha_2)\varphi_{2,m}\right)\right] \left[5\sqrt{\pi} + \lambda_2 \sqrt{2} exp(-\alpha_2 \varphi_{2,m}) \left(1 + exp(\varphi_{2,m})\right)\right]^{-1} exp(-\varphi_{1,m})$$
(19)

$$W_m = 5\sqrt{\pi} \left[5\sqrt{\pi} + \lambda_2 \sqrt{2} exp(-\alpha_2 \varphi_{2,m}) \left(1 + exp(\varphi_{2,m})\right)\right]^{-1}$$
(20)

$$\lambda_i = k_{s,i}(Df)^{-1/2} \quad (i = 1, 2)$$
(21)

$$s_k = \sqrt{k} - \sqrt{k-1}$$
(22)

$$1 \le m \le M$$
(23)

$$M = 50\left(E_{start} - E_{final}\right)/dE$$
(24)

3. RESULTS AND DISCUSSION

If the intermediate is highly unstable ($E_2^0 - E_1^0 \ge 0.3$ V) and electron transfers of the electrode reactions (1) and (2) are fast and reversible, the net response in square-wave voltammetry does not depend on the scan direction and the starting potential. For both cathodic (dE = -5 mV) and anodic (dE = 5 mV) directions and for E_{SW} = 50 mV the dimensionless net peak currents $-\Delta\Phi_p$ and $\Delta\Phi_p$ are equal to 1.91 and the net peak potentials are equal to the median of standard potentials ($E_p = (E_1^0 + E_2^0)/2$). In both cases the forward component is bigger than the backward component. The peak potentials of reductive components are equal to $E_p + 0.005$ V and the peak potentials of oxidative components are equal to $E_p - 0.005$ V.
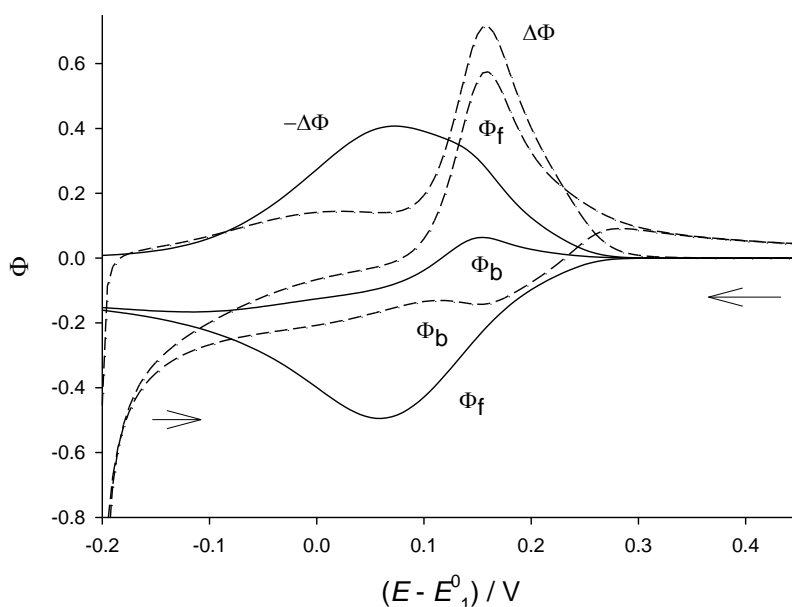

Figure 1. Square-wave voltammograms of electrode reactions (1) and (2). $E_2^0 - E_1^0 = 0.3$ V, $\lambda_1 = 1$, $\lambda_2 / \lambda_1 = 1000$, $\alpha_1 = 0.5$, $\alpha_2 = 0.5$, $E_{SW} = 50$ mV, $E_{st} = 0.5$ V *vs.* E_1^0 and dE = -5 mV (full lines) and $E_{st} = -0.2$ V *vs.* E_1^0 and dE = 5 mV (broken lines). The net responses (-$\Delta\Phi$ and $\Delta\Phi$) and their forward (Φ_f) and backward (Φ_b) components are shown.

The influence of the kinetics of the first electron transfer is shown in Figure 1. For the cathodic scan direction (full lines) the peak potential of the forward, reductive component is 0.060 V *vs.* E_1^0, which is lower than the reversible potential $(E_1^0 + E_2^0) / 2 = 0.150$ V *vs.* E_1^0. The backward component is in maximum at 0.155 V and the net peak potential is 0.075 V. The response to the reverse scan is dominated by the forward, oxidative component, which appears in maximum at 0.160 V (broken lines). The net peak potential and the potential of minimum of the backward component are 0.160 V and 0.150 V, respectively.
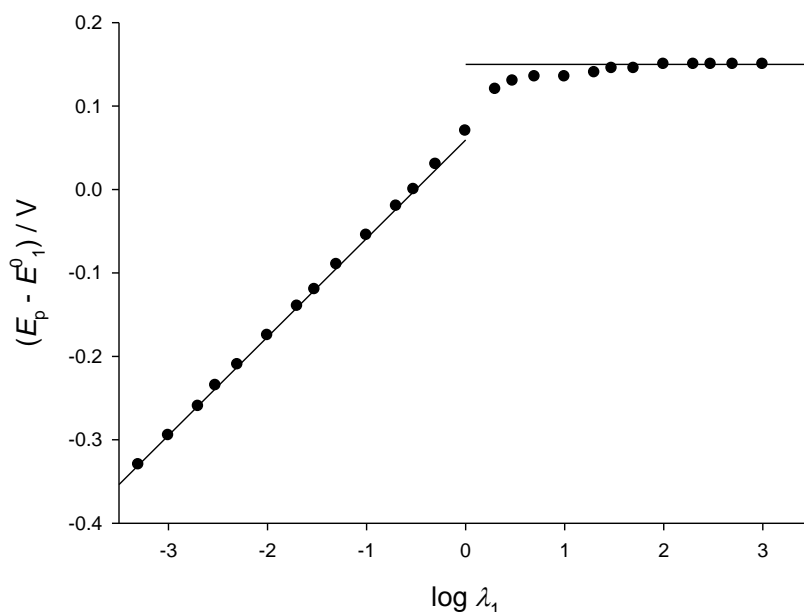

Figure 2. Dependence of net peak potentials on the logarithm of the first kinetic parameter. The straight lines are linear approximations. $E_2^0 - E_1^0 = 0.3$ V, $\lambda_2 / \lambda_1 = 10$, $\alpha_1 = 0.5$, $\alpha_2 = 0.3$, $E_{SW} = 50$ mV, $E_{st} = 0.5$ V *vs.* E_1^0 and d$E = -5$ mV.

Figure 2 shows the dependence of net peak potentials of the responses to the cathodic scan on the logarithm of kinetic parameter of the first electron transfer. If $\lambda_1 < 1$ this relationship is linear, with the slope $\Delta E_p / \Delta \log \lambda_1 = 2.3\, RT / \alpha_1 F$, where α_1 is the transfer coefficient of the first electron. This slope is independent of the transfer coefficient of the second electron. The same result was obtained for ten times faster transfer of the second electron ($\lambda_2 / \lambda_1 = 100$) and for all differences in standard potentials that are equal or bigger than zero. So, we can conclude that the net peak potential depends linearly on the logarithm of frequency, with the slope $\Delta E_p / \Delta \log f = -2.3\, RT / 2\alpha_1 F$, if $f > k_{s,1}^2 / D$, $k_{s,2} / k_{s,1} \geq 10$ and $E_2^0 - E_1^0 \geq 0$ V. This result is in agreement with the theory of cyclic voltammetry and chronoamperometry of two-step electroreduction mechanism which postulates that the slope of Tafel plot is equal to $-\alpha_1 F / RT$ (V^{-1}) if the first electron transfer is the rate determining step, and equal to $-(1+\alpha_2)F / RT$ (V^{-1}) if the second electron transfer is slower than the first one [29 - 31].

If the scan direction is anodic, the net response depends on the difference in standard potentials. Figure 3 shows the relationships that apply for $E_2^0 - E_1^0 > 0.1$ V. They are characterized by two

straight line segments that appear for $\log \lambda_1 < -2.5$ and $-2 < \log \lambda_1 < -0.5$, respectively. The slope of the first one is $\Delta E_p / \Delta \log \lambda_1 = -2.3\, RT / (1 - \alpha_2)F$, or $\Delta E_p / \Delta \log f = 2.3\, RT / 2(1 - \alpha_2)F$, which means that the second electron transfer is the rate determining step at these frequencies. The slope of the second segment is -0.040 ± 0.010 V and does not depend on the second transfer coefficient. Its origin cannot be explained at this point.
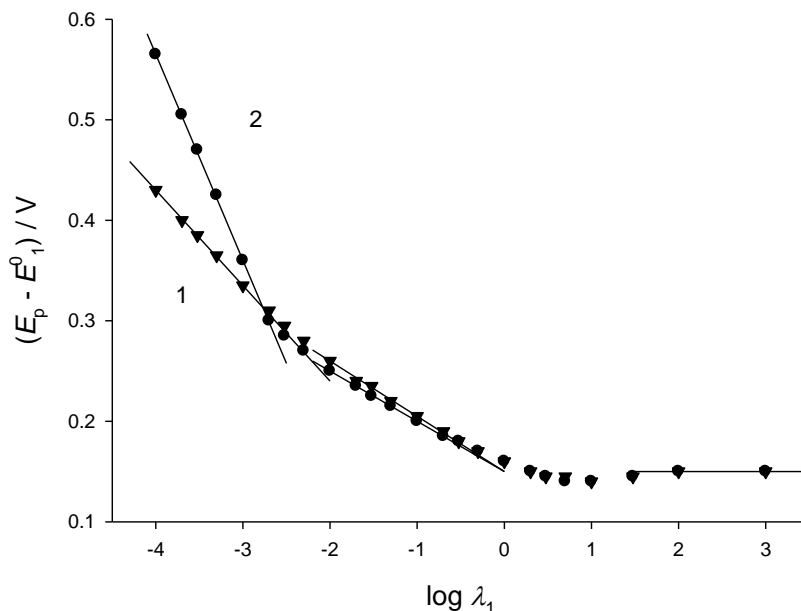

Figure 3. Dependence of net peak potentials on the logarithm of the first kinetic parameter. $E_2^0 - E_1^0 = 0.3$ V, $\lambda_2 / \lambda_1 = 100$, $\alpha_1 = 0.5$, $E_{SW} = 50$ mV, $E_{st} = -0.2$ V *vs.* E_1^0, $dE = 5$ mV and $\alpha_2 = 0.3$ (1) and 0.7 (2).
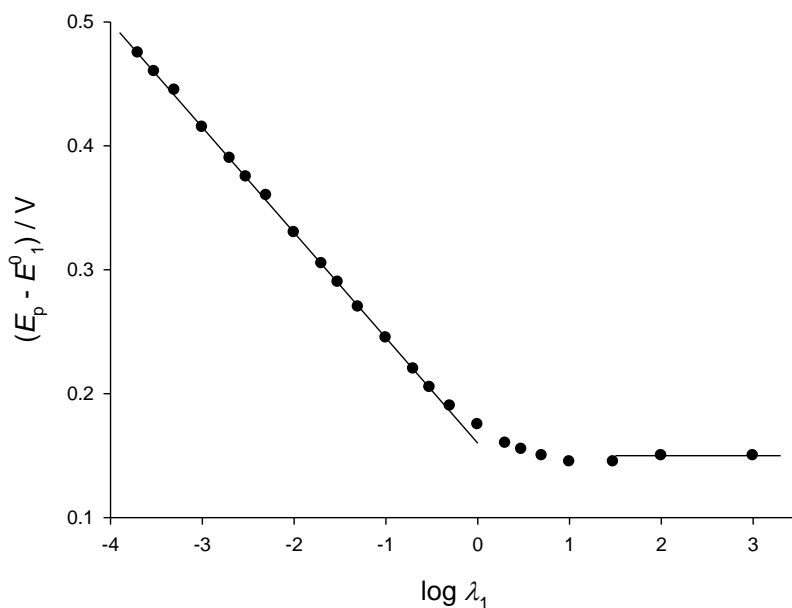

Figure 4. Dependence of net peak potentials on the logarithm of the first kinetic parameter. $E_2^0 - E_1^0 = 0.3$ V, $\lambda_2 / \lambda_1 = 10$, $\alpha_1 = 0.5$, $\alpha_2 = 0.3$, $E_{SW} = 50$ mV, $E_{st} = -0.2$ V *vs.* E_1^0 and $dE = 5$ mV.

However, this linear segment does not appear if $\lambda_2 / \lambda_1 = 10$ and $\alpha_2 < 0.6$. An example is shown in Figure 4, in which only the first linear relationship appears. Under these conditions the determination of α_2 is easier. The difference between curve (1) in Figure 3 and Figure 4 is smaller ratio λ_2 / λ_1 in the latter. The first electrode reaction is totally irreversible if $\lambda_1 < 1$, as can be seen in Figure 2, so that the second electrode reaction is totally irreversible if either $\lambda_1 < 10^{-2}$, if $\lambda_2 / \lambda_1 = 100$, or $\lambda_1 < 0.1$ for $\lambda_2 / \lambda_1 = 10$. Hence, it is most probable that the second linear segment in Figure 3 corresponds to the range of frequencies in which the second electrode reaction is quasireversible.
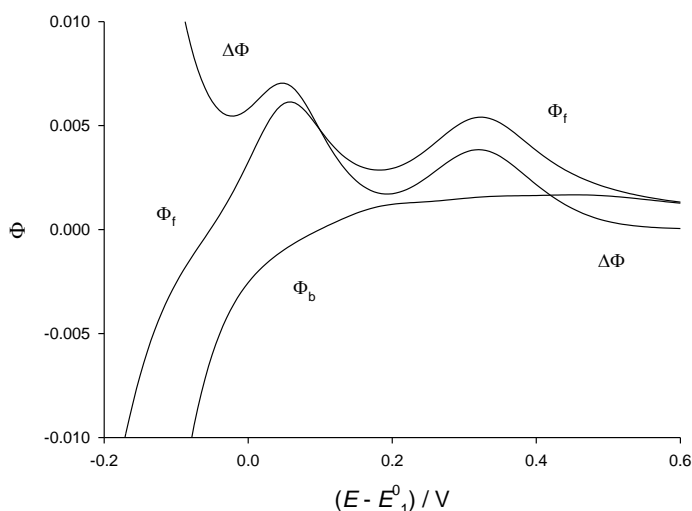

Figure 5. Square-wave voltammogram of electrode reactions (1) and (2). $E_2^0 = E_1^0$, $\lambda_1 = 5 \times 10^{-4}$, $\lambda_2 / \lambda_1 = 100$, $\alpha_1 = 0.5$, $\alpha_2 = 0.3$, $E_{SW} = 50$ mV, $E_{st} = -0.2$ V *vs.* E_1^0 and $dE = 5$ mV.

Figure 5 shows that the response to the inverse scan may split into two peaks if the intermediate is kinetically stabilized. The condition is that $E_2^0 - E_1^0 < 0.1$ V. The first peak, at lower potential, corresponds to the second electron transfer and the second peak is caused by the first electron transfer.
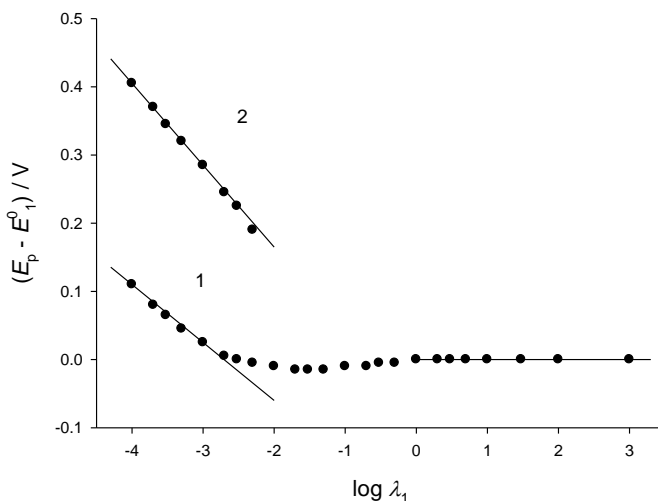

A
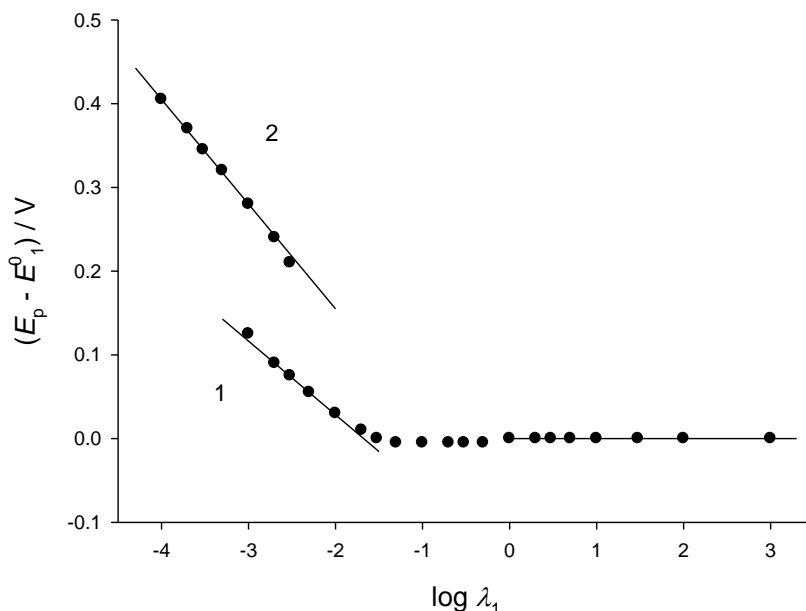
B

Figure 6. Dependence of potentials of maxima of the first (1) and the second (2) peak on the logarithm of the first kinetic parameter. $E_2^0 = E_1^0$, $\alpha_1 = 0.5$, $\alpha_2 = 0.3$, $E_{SW} = 50$ mV, $E_{st} = -0.2$ V *vs.* E_1^0, d$E = 5$ mV and $\lambda_2 / \lambda_1 = 100$ (A) and 10 (B).

This is confirmed by the relationships between peak potentials of the first and the second peak and the logarithm of the first kinetic parameter, which are shown in Figure 6. The slopes of straight lines 1 and 2 in this figure are $\Delta E_{p,1} / \Delta \log \lambda_1 = -2.3\, RT / (1 - \alpha_2)F$ and $\Delta E_{p,2} / \Delta \log \lambda_1 = -2.3\, RT / (1 - \alpha_1)F$.

If $E_2^0 - E_1^0 = 0.1$ V both types of response may appear, as can be seen in Figure 7. If $\alpha_2 = 0.3$ the net response is dominated by the first peak if $\log \lambda_1 > -3$ and the second peak if $\log \lambda_1 < -3$. The dependence of E_p on $\log \lambda_1$ exhibits two straight lines with the slopes as in Figure 6.
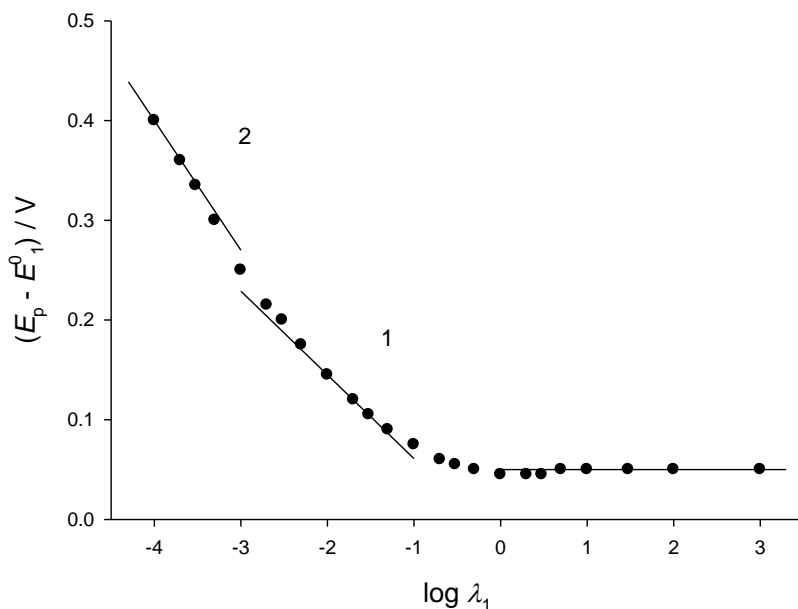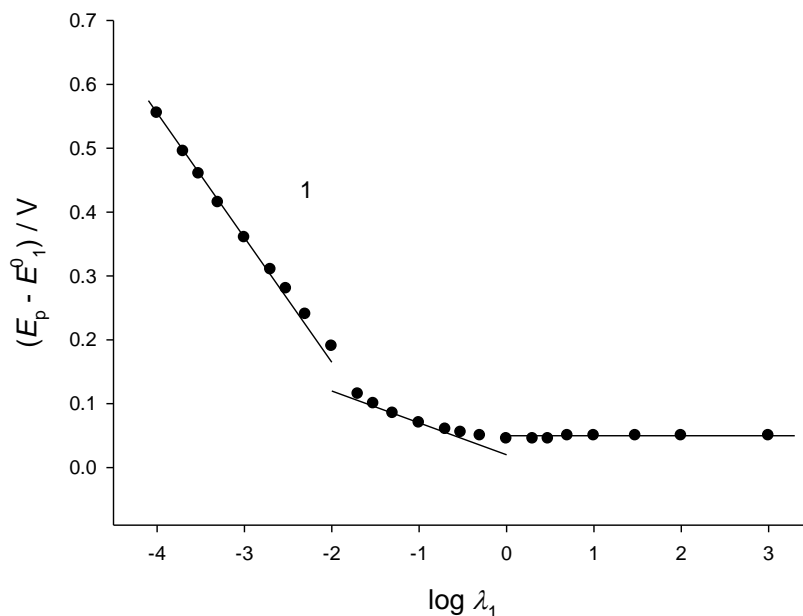

A

Figure 7. Dependence of net peak potentials on the logarithm of the first kinetic parameter. $E_2^0 - E_1^0 = 0.1$ V, $\lambda_2 / \lambda_1 = 10$, $\alpha_1 = 0.5$, $E_{SW} = 50$ mV, $E_{st} = -0.2$ V *vs.* E_1^0, $dE = 5$ mV and $\alpha_2 = 0.3$ (A) and 0.7 (B).

However, these peaks are mutually merged and not as separated as for $E_2^0 = E_1^0$. If $\alpha_2 = 0.7$ only the first peak appears, as in Figure 3. The slopes of linear segments in Figure 7B are $\Delta E_p / \Delta \log\lambda_1 = -2.3 \, RT / (1 - \alpha_2)F$ and -0.050 V, respectively. This shows that the second transfer coefficient can be determined easier if the intermediate is not kinetically stabilized. The stability is diminished if the transfer coefficient of oxidation $(1 - \alpha_2)$ of the species Red^{p+} is lower.

4. CONCLUSIONS

Transfer coefficients of the two-step electrode reaction in which the first electron transfer is rate determining step can be measured by square-wave voltammetry using cathodic and anodic scan directions. The first direction serves for the characterization of the first charge transfer, while the second electrode reaction can be analyzed by the reverse scan. In the latter case it is better that intermediate is stabilized neither thermodynamically nor kinetically and that the second electron transfer is less than thousand times faster than the first one. The relationships between peak potentials and the logarithm of frequency depend on the transfer coefficients α_1 and α_2, and not on the products $\alpha_1 n$ and $\alpha_2 n$, where $n = 2$.

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Meanings of symbols:

α_1, α_2 The transfer coefficients of the first and the second electron transfer steps

c_{Ox}, c_{Int}, c_{Red} The concentrations of the reactant, intermediate and the product

c_{Ox}^* The concentration of the reactant in the bulk of solution

D The common diffusion coefficient

dE The square-wave potential increment

E The electrode potential

E_1^0, E_2^0 The standard potentials of the first and the second electron transfer steps

E_{sw} The square-wave amplitude

E_{st} The square-wave starting potential

E_p The peak potential

$E_{p,f}$, $E_{p,b}$ The peak potentials of the forward and backward components

F	The Faraday constant
f	The square-wave frequency
Φ	The dimensionless current
$\Delta\Phi_p$	The dimensionless net peak current
I	The current
ΔI	The net square-wave voltammetric response
I_f, I_b	The forward and backward currents
ΔI_p	The net peak current
k_{s1}, k_{s2}	The standard rate constants of the first and the second electron transfer steps
λ_1, λ_2	The dimensionless kinetic parameters of the first and the second electrons
R	The gas constant
S	The electrode surface area
t	The time
x	The distance perpendicular to the electrode surface