



Theory of square wave voltammetry of three step electrode reaction



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ABSTRACT

A theory of square wave voltammetry of three step electrode reaction of amalgam forming ions is developed for a thin mercury film electrode. It is assumed that the first and the second electron transfers are kinetically controlled while the third one is reversible and that the intermediates are thermodynamically unstable. The responses to the cathodic and anodic scan directions are analyzed.

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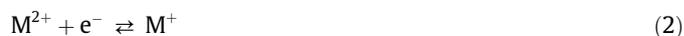
1. Introduction

The exchange of three electrons between an electrode and a redox center can occur in three consecutive steps if the center contains three electronic levels that can accommodate one electron each [1–3]. In voltammetry the response may consist of one, two or three peaks, depending on the stability of intermediates [4,5]. The theory of this type of reactions is developed for the single and double pulse chronoamperometry [6–8], chronopotentiometry [9,10], polarography [11–13], cyclic voltammetry [14–16] and square wave voltammetry [17]. Electrode reactions of bismuth [18–26] and antimony [27] were analyzed. The responses of charge transfers that are kinetically controlled depend on the standard rate constants and transfer coefficients of all slow steps [6,11,12,15,17]. Under these conditions the intermediates could be additionally stabilized by the electrode kinetics and the form of response may change with the frequency or scan rate [17]. In this paper electrode reactions that are influenced by the kinetics of the first and the second step are analyzed theoretically 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 [28,29]. The possibility to determine the second transfer coefficient is investigated.

2. The model

An electrode reaction that occurs through three consecutive steps is analyzed. It is assumed that the final product is an atom

that is dissolved into a thin mercury film that covers a stationary working electrode surface and that only the reactant M^{3+} is initially present in the solution. Furthermore, we assume that the first two charge transfers are kinetically controlled while the third one is fast and reversible. The rates of electron transfers are described by well established Butler–Volmer equation, assuming that transfer coefficients may vary between 0.25 and 0.75 [1,6,12,15,16].



The uniform concentration of atoms in the thin film is assumed. For the stationary, semi-infinite diffusion of ions, the following system of differential equations has to be solved:

$$\partial c_{M^{3+}} / \partial t = D(\partial^2 c_{M^{3+}} / \partial x^2) \quad (4)$$

$$\partial c_{M^{2+}} / \partial t = D(\partial^2 c_{M^{2+}} / \partial x^2) \quad (5)$$

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

$$t = 0, x \geq 0: c_{M^{3+}} = c_{M^{3+}}^*, c_{M^{2+}} = c_{M^+} = c_{M^0} = 0 \quad (7)$$

$$t > 0, x \rightarrow \infty: c_{M^{3+}} \rightarrow c_{M^{3+}}^*, c_{M^{2+}} \rightarrow 0, c_{M^+} \rightarrow 0 \quad (8)$$

$$x = 0: D(\partial c_{M^{3+}} / \partial x)_{x=0} = -I_1 / FS \quad (9)$$

$$D(\partial c_{M^{2+}} / \partial x)_{x=0} = (I_1 - I_2) / FS \quad (10)$$

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$$D(\partial C_{M^+}/\partial x)_{x=0} = (I_2 - I_3)/FS \quad (11)$$

$$C_{M^0} = -L^{-1} \int_0^t (I_3/FS) d\tau \quad (12)$$

$$I_1/FS = -k_{s1} \exp(-\alpha_1 \varphi_1) [(C_{M^{3+}})_{x=0} - (C_{M^{2+}})_{x=0} \exp(\varphi_1)] \quad (13)$$

$$I_2/FS = -k_{s2} \exp(-\alpha_2 \varphi_2) [(C_{M^{2+}})_{x=0} - (C_{M^+})_{x=0} \exp(\varphi_2)] \quad (14)$$

$$(C_{M^+})_{x=0} = C_{M^0} \exp(\varphi_3) \quad (15)$$

$$\varphi_1 = (F/RT)(E - E_1^0) \quad (16)$$

$$\varphi_2 = (F/RT)(E - E_2^0) \quad (17)$$

$$\varphi_3 = (F/RT)(E - E_3^0) \quad (18)$$

The meanings of all symbols are reported in Table 1. Differential Eqs. (4)–(6) are solved by Laplace transformations and by the method of numerical integration proposed by Olmstead and Nicholson [30]. The solution is the system of recursive formulae for the dimensionless current, $\Phi_i = I_i(FSC_{M^{3+}})^{-1}(Df)^{-1/2}$, where $i = 1, 2$ or 3 . The sum, $\Phi = \Phi_1 + \Phi_2 + \Phi_3$ is reported as a function of electrode potential.

$$\Phi_{1,1} = -5\sqrt{\pi/2}\kappa_1 \exp(-\alpha_1 \varphi_{1,1}) [5\sqrt{\pi/2} + Z_3]^{-1} \quad (19)$$

$$\Phi_{1,m} = \left[-5\sqrt{\pi/2}\kappa_1 \exp(-\alpha_1 \varphi_{1,m}) - Z_3 \sum_{j=1}^{m-1} \Phi_{1j} s_{m-j+1} + Z_4 \sum_{j=1}^{m-1} \Phi_{2j} s_{m-j+1} + Z_5 \left(\sum_{j=1}^{m-1} \Phi_{3j} s_{m-j+1} - \sum_{j=1}^{m-1} \Phi_{3j} \right) \right] (5\sqrt{\pi/2} + Z_3)^{-1} \quad (20)$$

$$\Phi_{2,1} = \kappa_2 \exp(-\alpha_2 \varphi_{2,1}) Z_2^{-1} \Phi_{1,1} \quad (21)$$

$$\Phi_{2,m} = \kappa_2 \exp(-\alpha_2 \varphi_{2,m}) Z_2^{-1} \left(\Phi_{1,m} + \sum_{j=1}^{m-1} \Phi_{1j} s_{m-j+1} \right) - Z_6 \sum_{j=1}^{m-1} \Phi_{2j} s_{m-j+1} + Z_7 \left(\sum_{j=1}^{m-1} \Phi_{3j} s_{m-j+1} - \sum_{j=1}^{m-1} \Phi_{3j} \right) \quad (22)$$

$$\Phi_{3,1} = \Phi_{2,1} (1 + Z_1)^{-1} \quad (23)$$

$$\Phi_{3,m} = \left[\Phi_{2,m} + \sum_{j=1}^{m-1} \Phi_{2j} s_{m-j+1} - \sum_{j=1}^{m-1} \Phi_{3j} s_{m-j+1} - Z_1 \sum_{j=1}^{m-1} \Phi_{3j} \right] (1 + Z_1)^{-1} \quad (24)$$

$$Z_1 = \lambda \sqrt{\pi/200} \exp(\varphi_{3,m}) \quad (25)$$

$$Z_2 = 5\sqrt{\pi/2} + \kappa_2 \exp(-\alpha_2 \varphi_{2,m}) [1 + Z_1 \exp(\varphi_{2,m}) (1 + Z_1)^{-1}] \quad (26)$$

$$Z_3 = \kappa_1 \exp(-\alpha_1 \varphi_{1,m}) [1 + \exp(\varphi_{1,m}) (1 - \kappa_2 \exp(-\alpha_2 \varphi_{2,m}) Z_2^{-1})] \quad (27)$$

$$Z_4 = \kappa_1 \exp((1 - \alpha_1) \varphi_{1,m}) [1 - \kappa_2 Z_2^{-1} \exp(-\alpha_2 \varphi_{2,m}) (1 + Z_1 \exp(\varphi_{2,m}) (1 + Z_1)^{-1})] \quad (28)$$

$$Z_5 = \kappa_1 \kappa_2 Z_1 Z_2^{-1} \exp((1 - \alpha_1) \varphi_{1,m}) \exp((1 - \alpha_2) \varphi_{2,m}) (1 + Z_1)^{-1} \quad (29)$$

$$Z_6 = \kappa_2 Z_2^{-1} \exp(-\alpha_2 \varphi_{2,m}) [1 + \exp(\varphi_{2,m}) Z_1 (1 + Z_1)^{-1}] \quad (30)$$

$$Z_7 = \kappa_2 \exp((1 - \alpha_2) \varphi_{2,m}) Z_1 Z_2^{-1} (1 + Z_1)^{-1} \quad (31)$$

$$\lambda = L^{-1} \sqrt{D/f} \quad (32)$$

$$\kappa_i = k_{s,i} (Df)^{-1/2} \quad (i = 1, 2) \quad (33)$$

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

$$2 \leq m \leq M \quad (35)$$

$$M = 50(E_{st} - E_{fin})/dE \quad (36)$$

Table 1
Meanings of symbols.

α_1, α_2	Transfer coefficients of the first and the second electron transfer steps
$C_{M^{3+}}, C_{M^{2+}}, C_{M^+}, C_{M^0}$	Concentrations of the reactant, intermediates and the product
$C_{M^{3+}}^*$	Concentration of the reactant in the bulk of solution
D	Common diffusion coefficient
dE	Square wave potential increment
E	Electrode potential
E_1^0, E_2^0, E_3^0	Standard potentials of the first, the second and the third electron transfer steps
E_{sw}	Square wave amplitude
E_{st}	Square wave starting potential
E_p	Peak potential
F	Faraday constant
f	Square wave frequency
Φ	Dimensionless current
I_1, I_2, I_3	Currents of the first, the second and the third electron transfers
$k_{s,1}, k_{s,2}$	Standard rate constants of the first and the second electron transfers
κ_2, κ_1	Dimensionless kinetic parameters of the first and the second electron transfers
L	Mercury film thickness
λ	Dimensionless mercury film thickness
R	Gas constant
S	Electrode surface area
T	Temperature
t	Time
x	Distance perpendicular to the electrode surface

3. Results and discussion

If all three electron transfers are fast and reversible, the net response in square wave voltammetry may consist of either one peak, or two peaks, or three peaks. The single peak appears if $E_2^0 - E_1^0 > -0.1$ V and $E_3^0 - E_1^0 > -0.1$ V. This means that both intermediates are thermodynamically unstable. In the second case either the first, or the second intermediate is stable. These responses occur if $-0.2 < E_2^0 - E_1^0 < -0.1$ V and $-0.3 < E_3^0 - E_1^0 \leq 0$ V, or $E_2^0 - E_1^0 > -0.1$ V and $E_3^0 - E_1^0 < -0.1$ V. The last type of voltammogram arise if $E_2^0 - E_1^0 < -0.2$ V and $E_3^0 - E_2^0 < -0.1$ V. The peak potentials are equal to the standard potentials, except for the third one that depends on the logarithm of dimensionless mercury film thickness: $E_{p,3} = E_3^0 - 0.040 - (RT/F) \ln(\lambda)$ (V). For this reason the potential of a single peak is also the function of the parameter λ : $E_p = (E_1^0 + E_2^0 + E_3^0)/3 - 0.040 - (RT/3F) \ln(\lambda)$ (V). All these responses do not depend on the scan direction and the starting potential. In this paper it is assumed that standard potentials are equal: $E_1^0 = E_2^0 = E_3^0$.

Fig. 1 shows the voltammogram influenced by the kinetics of the first electron transfer. For the cathodic scan direction the response is dominated by the forward, reductive component, while the backward component gradually vanishes. The dependence of net peak potentials on the logarithm of the first dimensionless kinetic parameter is shown in Fig. 2A. If $\log(\kappa_1) < -2$ this relationship is

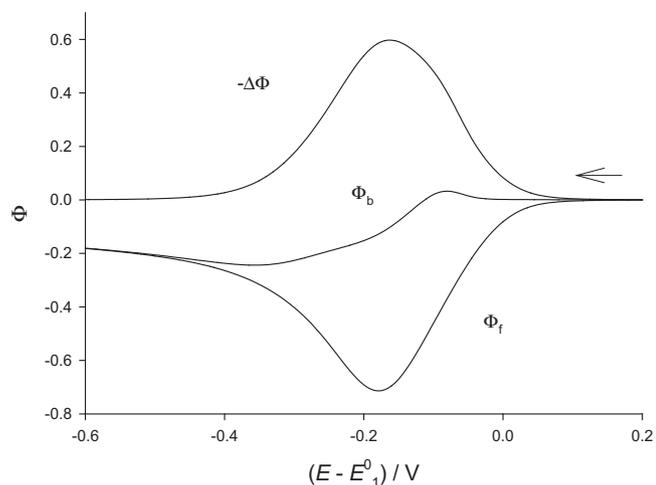


Fig. 1. Theoretical square wave voltammogram of electrode reactions (1)–(3). A negative value of the dimensionless net response ($-\Delta\Phi$) and its forward (Φ_f) and backward (Φ_b) components are shown. $E_1^0 = E_2^0 = E_3^0$, $\alpha_1 = 0.5$, $\alpha_2 = 0.3$, $\lambda = 3$, $\kappa_2/\kappa_1 = 100$, $\kappa_1 = 0.01$, $E_{sw} = 50$ mV, $dE = -5$ mV and $E_{st} = 0.2$ V vs. E_1^0 .

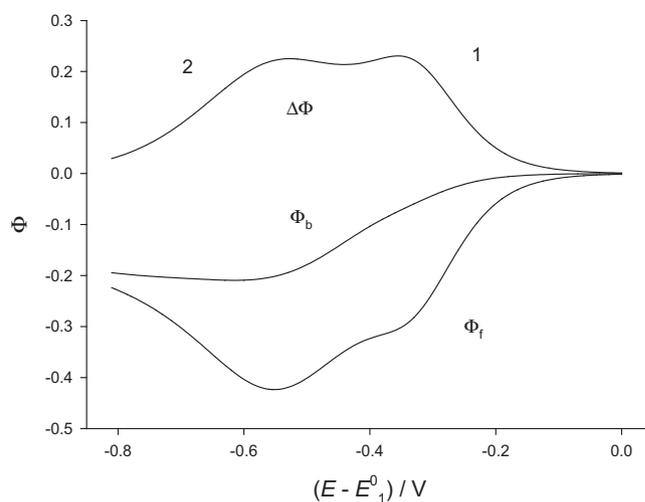


Fig. 3. Square wave voltammogram of reactions (1)–(3). $\kappa_2 = \kappa_1$, $E_{st} = 0$ V vs. E_1^0 , $\alpha_2 = 0.3$ and $\kappa_1 = 5 \times 10^{-4}$. All other parameters are as in Fig. 1.

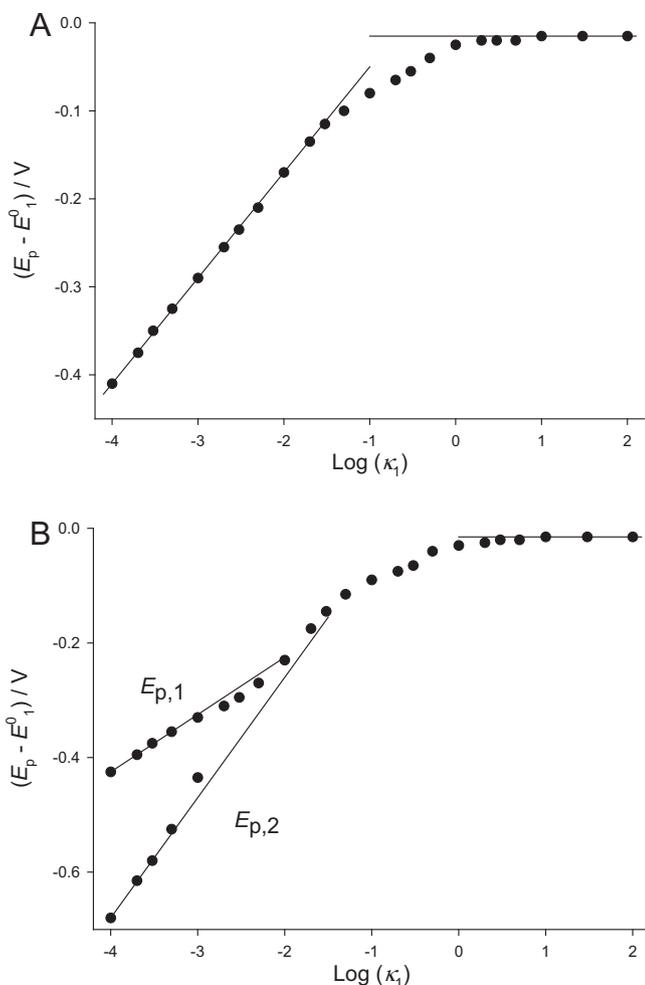


Fig. 2. Relationships between net peak potentials and the logarithm of the first kinetic parameter. The straight lines are linear approximations. $\kappa_2 = \kappa_1$ and $\alpha_2 = 0.7$ (A) and 0.3 (B). All other parameters are as in Fig. 1.

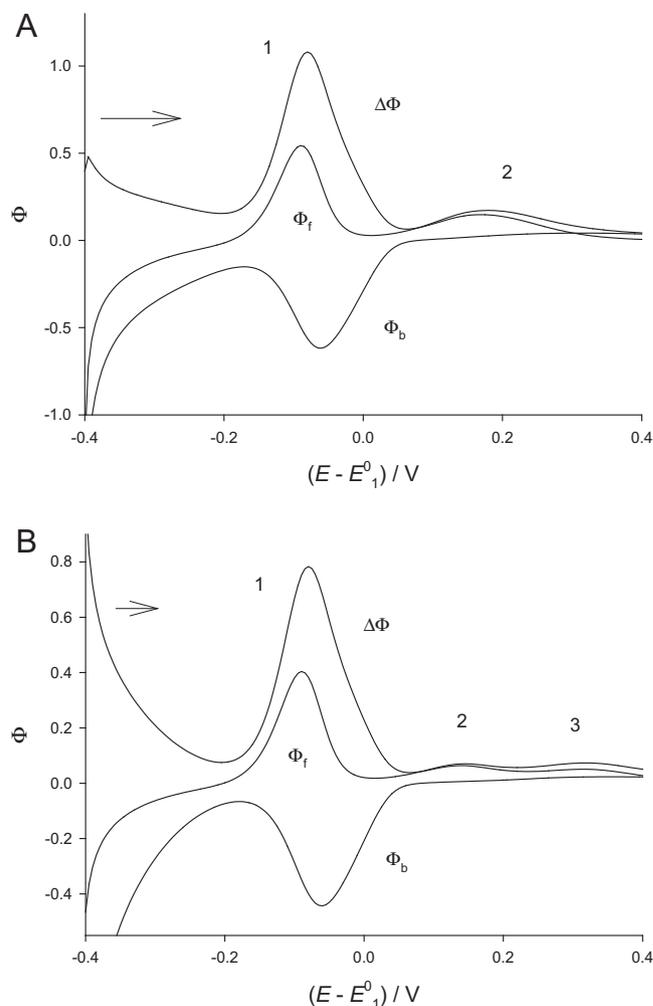


Fig. 4. Reverse scan square wave voltammograms of reactions (1)–(3). $E_1^0 = E_2^0 = E_3^0$, $\alpha_1 = 0.5$, $\alpha_2 = 0.3$, $\lambda = 3$, $E_{sw} = 50$ mV, $dE = 5$ mV and $E_{st} = -0.4$ V vs. E_1^0 . (A) $\kappa_2 = \kappa_1$ and $\kappa_1 = 5 \times 10^{-3}$. (B) $\kappa_2/\kappa_1 = 10$ and $\kappa_1 = 5 \times 10^{-4}$. The first, the second and the third peak are marked as 1, 2 and 3.

linear, with the slope $\Delta E_p/\Delta\log(\kappa_1) = 2.3 RT/\alpha_1 F$. This slope is independent of the transfer coefficient of the second electron if $\kappa_2 \geq \kappa_1$, $E_2^0 \geq E_1^0$ and $E_3^0 \geq E_1^0$. However, if the first intermediate is kinetically stabilized, the response may split into two peaks. An example is shown in Fig. 3. It corresponds to equal standard rate constants of the first and the second electron transfers, but the transfer coefficient of the second electron transfer step is assumed to be smaller than the transfer coefficient of the first step. Under this condition both transfer coefficients can be determined from the slopes $\Delta E_{p,1}/\Delta\log(\kappa_1) = 2.3 RT/\alpha_1 F$ and $\Delta E_{p,2}/\Delta\log(\kappa_2) = 2.3 RT/\alpha_2 F$, as can be seen in Fig. 2B. The second equation is the consequence of the fact that in this figure $\kappa_2 = \kappa_1$. Considering the definitions of kinetic parameters, these equations indicate the relationships between peak potentials and square wave frequency: $\Delta E_{p,1}/\Delta\log(f) = -2.3 RT/2\alpha_1 F$ and $\Delta E_{p,2}/\Delta\log(f) = -2.3 RT/2\alpha_2 F$.

If the reverse scan is applied, the response may split into two or three peaks. This is shown in Fig. 4. The first peak originates from the reversible oxidation of amalgam into M^+ intermediate. This is indicated by well developed backward, reductive component of this peak. The other two oxidations appear totally irreversible. Fig. 5 shows the relationships between peak potentials and the logarithm of the first kinetic parameter for the case of equal kinetic parameters. This figure corresponds to voltammograms that consist of only two peaks, as the one in Fig. 4A. The first peak potential is independent of the kinetic parameter because it is assumed that

this electron transfer is fast and reversible. Within the range $-1 < \log(\kappa_1) < 1$ this peak corresponds to quasireversible transfer of all three electrons. If $\log(\kappa_1) < -1.5$ the second peak appears. Its potential is linear function of $\log(\kappa_1)$. In Fig. 5A the slope of this straight line is $\Delta E_{p,2}/\Delta\log(\kappa_1) = -2.3 RT/(1 - \alpha_1)F$ and in Fig. 5B the slope is $\Delta E_{p,2}/\Delta\log(\kappa_2) = -2.3 RT/(1 - \alpha_2)F$. This is because in the first case $\alpha_1 > \alpha_2$ and in the second one $\alpha_2 > \alpha_1$. The slope depends on the slower oxidation and for $\kappa_2 = \kappa_1$ the third oxidation is the rate determining step if $1 - \alpha_1 < 1 - \alpha_2$. The consequence is that from this type of response one cannot know which transfer coefficient, α_1 or α_2 , is determined. Reverse scan voltammograms with two peaks also appear if $\kappa_2/\kappa_1 = 100$ and in this case the slope $\Delta E_{p,2}/\Delta\log(\kappa_1) = -2.3 RT/(1 - \alpha_1)F$ is independent of α_2 because the range of frequency is limited and the second kinetic parameter is varied only within the quasireversible range. This means that by the application of anodic scan direction the transfer coefficient α_1 of the first electron transfer is the most probably determined, as in the case of cathodic scan direction.

Voltammograms with three peaks are special case, which enables the determination of both transfer coefficients. They appear if $\kappa_2/\kappa_1 = 10$ and $\alpha_2 < \alpha_1$. Fig. 6A shows linear dependence of potentials of the second and the third peak on the logarithm of the first kinetic parameter. Note that $\log(\kappa_2) = 1 + \log(\kappa_1)$. The slopes of these relationships are $\Delta E_{p,2}/\Delta\log(\kappa_2) = -2.3 RT/(1 - \alpha_2)F$ and $\Delta E_{p,3}/\Delta\log(\kappa_1) = -2.3 RT/(1 - \alpha_1)F$. If $\alpha_2 > \alpha_1$ and

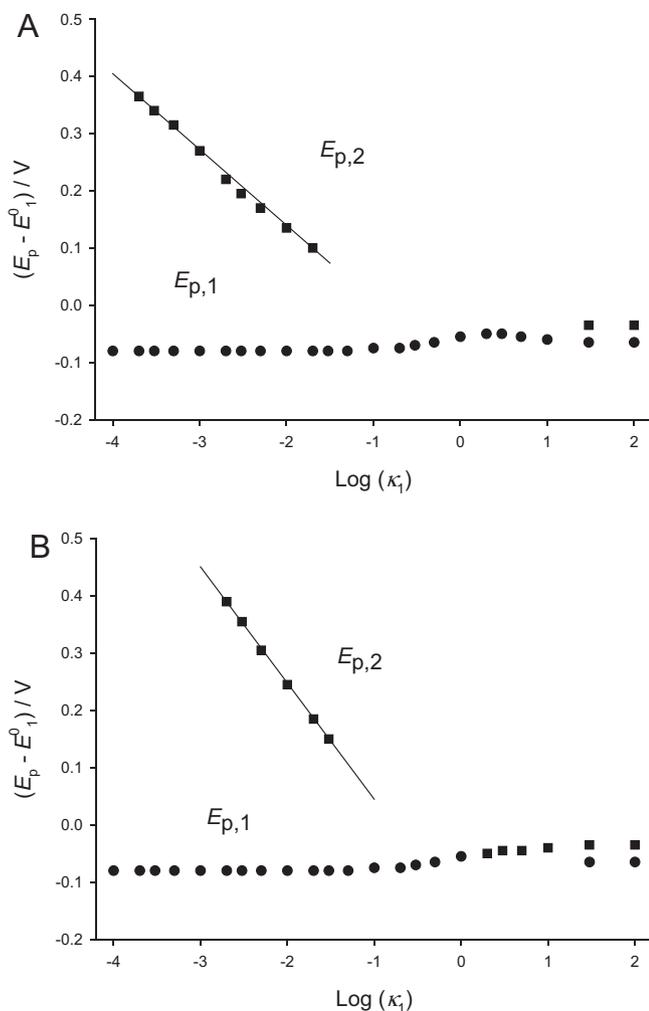


Fig. 5. Dependence of peak potentials on the logarithm of the first kinetic parameter; $\kappa_2 = \kappa_1$ and $\alpha_2 = 0.3$ (A) and 0.7 (B). All other parameters are as in Fig. 4.

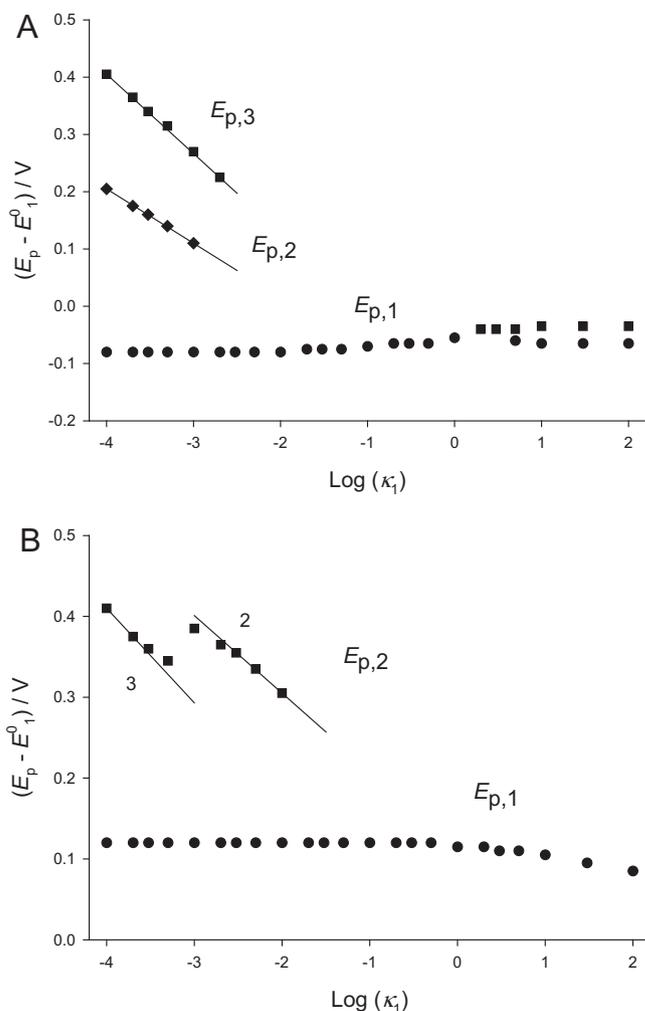


Fig. 6. Dependence of peak potentials on the logarithm of the first kinetic parameter. (A) $E_1^0 = E_2^0 = E_3^0$, $E_{st} = -0.4$ V vs. E_1^0 and $\kappa_2/\kappa_1 = 10$. (B) $E_2^0 = E_3^0$, $E_1^0 - E_2^0 = -0.2$ V, $E_{st} = -0.2$ V vs. E_1^0 and $\kappa_2 = \kappa_1$. Two asymptotes of the second peak are marked as 2 and 3. All other parameters are as in Fig. 4.

the other parameters are the same, the second and the third peaks merge into a single peak. Another special type of response is shown in Fig. 6B. It should be compared with Fig. 5A. The difference is in standard potentials that make intermediates thermodynamically less stable. In this case the second and third peaks are not separated, but the dependence of the second peak potential on $\log(\kappa_1)$ is not linear. Instead, it exhibits two asymptotes with the slopes $\Delta E_{p,2}/\Delta \log(\kappa_2) = -2.3 RT/(1 - \alpha_2)F$ and $\Delta E_{p,2}/\Delta \log(\kappa_1) = -2.3 RT/(1 - \alpha_1)F$. They are marked as 2 and 3 in Fig. 6B.

4. Conclusions

Square wave voltammetry can be used for the determination of transfer coefficients of the three step electrode reaction in which the first and second electron transfers are kinetically controlled and the intermediates are thermodynamically unstable. Generally, the relationship between peak potential and the logarithm of frequency depends on the first charge transfer, but in some special cases the responses split into two peaks and the second transfer coefficient can be determined as well. The condition is that the second coefficient is smaller than the first one.

Conflict of interest

The authors disclose that there is no conflict of interest that could influence this work.

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