

Simulation of Square Wave Voltammetry of Three Step Redox Reactions on Spherical Electrodes

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Abstract: The theory of three step electrode reaction is developed for square wave voltammetry on stationary spherical electrodes. It was assumed that all electroactive species are solution soluble. The dependence of the response on the thermodynamic stability of intermediates, on the electrode radius and the scan direction is investigated for the fast and reversible electrode reactions. The criterion of reversibility is postulated. Furthermore, the influence of electrode kinetics on the response was calculated for the cathodic and anodic scan directions. The difference in responses caused by the variation of scan direction is an indication of multiple electron transfers. The method for the estimation of transfer coefficient is demonstrated.

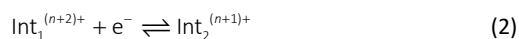
Keywords: square wave voltammetry, three step electrode reaction, theory, spherical electrode, kinetics of electrode reaction.

INTRODUCTION

ELECTRODE reactions that include three electrons may occur through three consecutive steps.^[1–6] The responses of this mechanism depend on the stability of intermediates and the kinetics of electron transfers.^[7–11] These relationships were calculated for chronoamperometry^[9,10,12–16] and voltammetry.^[11,17–20] They can be used for the determination of kinetic parameters.^[10,11,20–23] In this paper the theory is developed for kinetically controlled three step reaction on spherical electrodes. The purpose is to analyse the dependence of square wave voltammograms on the electrode radius and the signal frequency.^[1,12,14,24–28] The work is inspired by electrode reactions of uranyl,^[29] chromium(VI)^[30] and bis(fulvalene)dinickel^[31] ions and nitromethane^[32] and nitrobenzene^[33] on hemispherical microelectrodes.^[28]

THEORY

The model is developed under the assumption that all four components of the three step electrode reaction are solution soluble and that only the reactant $\text{Ox}^{(n+3)+}$ is initially present in the solution.



The mass transfer towards the surface of stationary spherical electrode is described by the following differential equation:

$$\partial c_Y / \partial t = D \partial^2 c_Y / \partial r^2 + (2D / r) \partial c_Y / \partial r \quad (4)$$

Here, the symbol Y stays for either $\text{Ox}^{(n+3)+}$ or $\text{Int}_1^{(n+2)+}$ or $\text{Int}_2^{(n+1)+}$ or Red^{n+} and the variable r is the radial distance from the centre of sphere. The starting and boundary conditions are the following:

$$t = 0, r \geq r_0 : c_{\text{Ox}} = c_{\text{Ox}}^*, c_{\text{Int}_1} = c_{\text{Int}_2} = c_{\text{Red}} = 0 \quad (5)$$

$$t > 0, r \rightarrow \infty : c_{\text{Ox}} \rightarrow c_{\text{Ox}}^*, \\ c_{\text{Int}_1} \rightarrow 0, c_{\text{Int}_2} \rightarrow 0, c_{\text{Red}} \rightarrow 0 \quad (6)$$

$$r = r_0 : D(\partial c_{\text{Ox}} / \partial r)_{r=r_0} = -I_1 / FS \quad (7)$$

$$D(\partial c_{\text{Int}_1} / \partial r)_{r=r_0} = (I_1 - I_2) / FS \quad (8)$$

$$D(\partial c_{\text{Int}_2} / \partial r)_{r=r_0} = (I_2 - I_3) / FS \quad (9)$$

$$D(\partial c_{\text{Red}} / \partial r)_{r=r_0} = I_3 / FS \quad (10)$$

$$I_1 / FS = -k_{s_1} \exp(-\alpha_1 \varphi_1) [(c_{\text{Ox}})_{r=r_0} - (c_{\text{Int}_1})_{r=r_0} \exp(\varphi_1)] \quad (11)$$

$$I_2 / FS = -k_{s_2} \exp(-\alpha_2 \varphi_2) [(c_{\text{Int}_1})_{r=r_0} - (c_{\text{Int}_2})_{r=r_0} \exp(\varphi_2)] \quad (12)$$

$$I_3 / FS = -k_{s_3} \exp(-\alpha_3 \varphi_3) [(c_{\text{Int}_2})_{r=r_0} - (c_{\text{Red}})_{r=r_0} \exp(\varphi_3)] \quad (13)$$

$$\varphi_1 = (F / RT)(E - E_1^0) \quad (14)$$

$$\varphi_2 = (F / RT)(E - E_2^0) \quad (15)$$

$$\varphi_3 = (F / RT)(E - E_3^0) \quad (16)$$

The symbol r_0 stays for the electrode radius and the meanings of all other symbols are reported in Table 1. Differential equations are solved by the numerical method proposed by Olmstead and Nicholson.^[34] The solution is the system of recursive formulae for the dimensionless current $\Phi_j = I_j (FSC_{\text{Ox}}^*)^{-1} (Df)^{-1/2}$, where $j = 1, 2$ or 3 . The sum $\Phi = \Phi_1 + \Phi_2 + \Phi_3$ is reported as a function of electrode potential.

$$\Phi_{2,m} = \frac{1}{Z_5} (-Z_1 + Z_2 \sum_{j=1}^{m-1} \Phi_{1,j} s_{m-j+1} + \dots + Z_3 \sum_{j=1}^{m-1} \Phi_{2,j} s_{m-j+1} + Z_4 \sum_{j=1}^{m-1} \Phi_{3,j} s_{m-j+1}) \quad (17)$$

$$\Phi_{1,m} = \frac{1}{1 + A_1 s_1} (-k_1 \exp(-\alpha_1 \varphi_1) + \dots + B_1 \sum_{j=1}^m \Phi_{2,j} s_{m-j+1} - A_1 \sum_{j=1}^{m-1} \Phi_{1,j} s_{m-j+1}) \quad (18)$$

$$\Phi_{3,m} = \frac{1}{1 + A_3 s_1} (-A_3 \sum_{j=1}^{m-1} \Phi_{3,j} s_{m-j+1} + C_3 \sum_{j=1}^m \Phi_{2,j} s_{m-j+1}) \quad (19)$$

$$\rho = D^{1/2} r_0^{-1} f^{-1/2} \quad (20)$$

$$\kappa_1 = k_{s_1} (Df)^{-1/2} \quad (21)$$

$$\lambda_j = k_{s_j} r_0 D^{-1} \quad (j = 1, 2 \text{ or } 3) \quad (22)$$

Table 1. Meanings of symbols.

Symbol	Meaning
$\alpha_1, \alpha_2, \alpha_3$	Transfer coefficients of the first, the second and the third electron transfer steps
$c_{\text{Ox}}, c_{\text{Int}_1}, c_{\text{Int}_2}, c_{\text{Red}}$	Concentrations of the reactant, two intermediates and the product
C_{Ox}^*	Concentration of the reactant in the bulk of solution
D	Common diffusion coefficient
dE	Square wave potential increment
E	Electrode potential
E_1, E_2, E_3	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_{fin}	Square wave final potential
E_p	Peak potential
F	Faraday constant
f	Square wave frequency
I_1, I_2, I_3	Currents of the first, the second and the third electron transfers
$k_{s_1}, k_{s_2}, k_{s_3}$	Standard rate constants of the first, the second and the third electron transfers
r_0	Electrode radius
R	Gas constant
ρ	Sphericity parameter defined by [Eq. (20)]
S	Electrode surface area
T	Temperature
t	Time

$$q = \rho^2 / 50 \quad (23)$$

$$s_1 = 1 - \exp(q) \operatorname{erfc} \sqrt{q} \quad (24)$$

$$s_p = \exp[q(p-1)] \operatorname{erfc} \sqrt{q(p-1)} - \exp(qp) \operatorname{erfc} \sqrt{qp} \quad (25)$$

$$A_1 = \lambda_1 \exp(-\alpha_1 \varphi_1) [1 + \exp(\varphi_1)] \quad (26)$$

$$A_2 = \lambda_2 \exp(-\alpha_2 \varphi_2) [1 + \exp(\varphi_2)] \quad (27)$$

$$A_3 = \lambda_3 \exp(-\alpha_3 \varphi_3) [1 + \exp(\varphi_3)] \quad (28)$$

$$B_1 = \lambda_1 \exp[(1 - \alpha_1) \varphi_1] \quad (29)$$

$$B_2 = \lambda_2 \exp[(1 - \alpha_2) \varphi_2] \quad (30)$$

$$C_2 = \lambda_2 \exp(-\alpha_2 \varphi_2) \quad (31)$$

$$C_3 = \lambda_3 \exp(-\alpha_3 \varphi_3) \quad (32)$$

$$Z_1 = \kappa_1 \exp(-\alpha_1 \varphi_1) C_2 s_1 (1 + A_1 s_1)^{-1} (1 + A_2 s_1)^{-1} \quad (33)$$

$$Z_2 = C_2 [1 - A_1 s_1 (1 + A_1 s_1)^{-1}] (1 + A_2 s_1)^{-1} \quad (34)$$

$$Z_3 = [B_1 C_2 s_1 (1 + A_1 s_1)^{-1} - A_2 + B_2 C_3 s_2 (1 + A_3 s_1)^{-1}] \cdot \dots \cdot (1 + A_2 s_1)^{-1} \quad (35)$$

$$Z_4 = B_2 [1 - A_3 s_1 (1 + A_3 s_1)^{-1}] (1 + A_2 s_1)^{-1} \quad (36)$$

$$Z_5 = 1 - [B_1 C_2 s_1^2 (1 + A_1 s_1)^{-1} + B_2 C_3 s_1^2 (1 + A_3 s_1)^{-1}] \cdot \dots \cdot (1 + A_2 s_1)^{-1} \quad (37)$$

$$1 \leq m \leq M \quad (38)$$

$$M = 50(E_{st} - E_{fin}) / dE \quad (39)$$

RESULTS AND DISCUSSION

Square wave voltammogram of electrode reaction in which all three electron transfers are fast and reversible depends on standard potentials of individual steps and the sphericity parameter $\rho = (D/f)^{1/2} / r_0$. An example is shown in Figure 1. It can be noted that the net response is independent of the scan direction. For equal standard potentials the net peak potential is equal to E_1 and the peak current is 5.33 in both figures 1A and 1B. This identity is the best indication of reversible electrode reaction. There is, however, a small difference between the minima and maxima of the components of these two voltammograms. If $E_{st} - E_1 = 0.3 \text{ V}$, $\Phi_{\text{Red,min}} = -4.51$, $E_{p,\text{Red}} - E_1 = -0.015 \text{ V}$, $\Phi_{\text{Ox,max}} = 0.90$ and $E_{p,\text{Ox}} - E_1 = 0.010 \text{ V}$, while for $E_{st} - E_1 = -0.3 \text{ V}$, $\Phi_{\text{Red,min}} = -4.12$, $E_{p,\text{Red}} - E_1 = -0.010 \text{ V}$, $\Phi_{\text{Ox,max}} = 1.30$ and $E_{p,\text{Ox}} - E_1 = 0.015 \text{ V}$. Also, the limiting current of components at $E - E_1 = -0.2 \text{ V}$ depends on the starting potential. This current is a consequence of spherical diffusion and depends on the parameter ρ . The net current is defined as a difference between the forward and the backward components. In the case of cathodic scan direction this difference is negative and the net current is defined as $-\Delta\Phi = \Phi_{\text{Ox}} - \Phi_{\text{Red}}$.

Tables 2 and 3 show the relationship between the form of response and the standard potentials of individual electron transfer steps. Again, the peak currents and peak potentials that are reported in these tables are all independent of the scan direction. If $E_2 - E_1 = 0.1 \text{ V}$ and $E_3 - E_1 = 0.2 \text{ V}$ the response consists of a single peak with the maximum at $E_p - E_1 = (E_2 + E_3) / 3$. This rule applies if

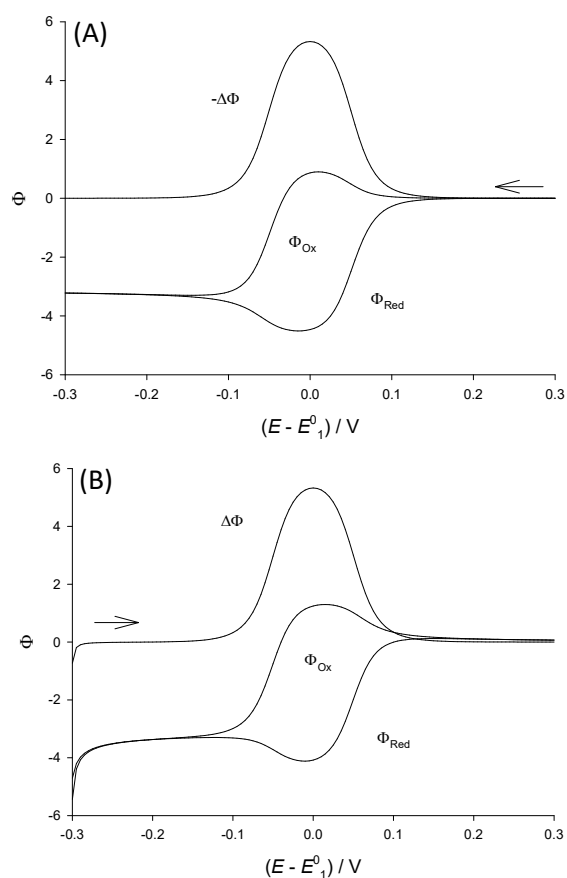


Figure 1. Dimensionless square wave voltammograms of reversible three step electrode reaction. A net peak current ($-\Delta\Phi$ or $\Delta\Phi$) and its reductive (Φ_{Red}) and oxidative (Φ_{Ox}) components are shown. $E_3 = E_2 = E_1$, $\rho = 1$, $E_{\text{SW}} = 50 \text{ mV}$, $dE = -5 \text{ mV}$ (A) and 5 mV (B), $E_{\text{st}} - E_1 = 0.3 \text{ V}$ (A) and -0.3 V (B).

Table 2. Dependence of dimensionless net peak currents and peak potentials on the difference between standard potentials of electron transfer steps; $E_3 - E_2 = E_2 - E_1$ and $\rho = 0.1$.

$\frac{E_2 - E_1}{V}$	$-\Delta\Phi_{p,1}$	$\frac{E_{p,1} - E_1}{V}$	$-\Delta\Phi_{p,2}$	$\frac{E_{p,2} - E_1}{V}$	$-\Delta\Phi_{p,3}$	$\frac{E_{p,3} - E_1}{V}$
0.100	3.253	0.100	—	—	—	—
0.050	3.207	0.050	—	—	—	—
0.000	2.930	0.000	—	—	—	—
-0.050	1.986	-0.050	—	—	—	—
-0.100	1.109	-0.085	—	—	—	—
-0.120	0.914	-0.015	0.966	-0.120	0.918	-0.225
-0.130	0.882	-0.010	0.923	-0.130	0.885	-0.250
-0.140	0.863	-0.005	0.893	-0.140	0.865	-0.275
-0.150	0.850	-0.005	0.873	-0.150	0.852	-0.295
-0.200	0.830	0.000	0.834	-0.200	0.831	-0.400

Table 3. Dependence of dimensionless net peak currents and peak potentials on the difference between standard potentials of electron transfer steps; $E_2 - E_1 = -0.2$ V and $\rho = 0.1$.

$\frac{E_3 - E_2}{V}$	$-\Delta\Phi_{p,1}$	$\frac{E_{p,1} - E_1}{V}$	$-\Delta\Phi_{p,2}$	$\frac{E_{p,2} - E_1}{V}$	$-\Delta\Phi_{p,3}$	$\frac{E_{p,3} - E_1}{V}$
0.100	0.831	0.000	2.088	-0.150	–	–
0.050	0.830	0.000	2.010	-0.175	–	–
0.000	0.830	0.000	1.856	-0.200	–	–
-0.050	0.830	0.000	1.549	-0.225	–	–
-0.100	0.830	0.000	1.080	-0.250	–	–
-0.110	0.830	0.000	0.977	-0.240	0.979	-0.275
-0.120	0.830	0.000	0.917	-0.215	0.918	-0.305
-0.130	0.830	0.000	0.885	-0.210	0.885	-0.320
-0.150	0.830	0.000	0.854	-0.205	0.852	-0.345
-0.200	0.830	0.000	0.834	-0.200	0.831	-0.400

$E_3 - E_2 = E_2 - E_1$ and $E_2 - E_1 > -0.1$ V. The peak current decreases with the diminishing difference $E_2 - E_1$ because the half-peak width increases. Figure 2 shows the response in the form of mesa that appears if $E_2 - E_1 = -0.11$ V and $E_3 - E_1 = -0.22$ V. It is characterized by $-\Delta\Phi_p = 1.03$ and $E_p - E_1 = -0.11$ V. With the further decrement of the difference $E_2 - E_1$ the response with three peaks appear. If $E_2 - E_1 < -0.15$ V and $E_3 - E_1 < -0.3$ V the peak potentials are equal to standard potentials.

The response with two peaks may appear if one of intermediates is thermodynamically stable. If $E_2 - E_1 = -0.2$ V the first electron transfer is not influenced by the other two transfers. The second peak corresponds

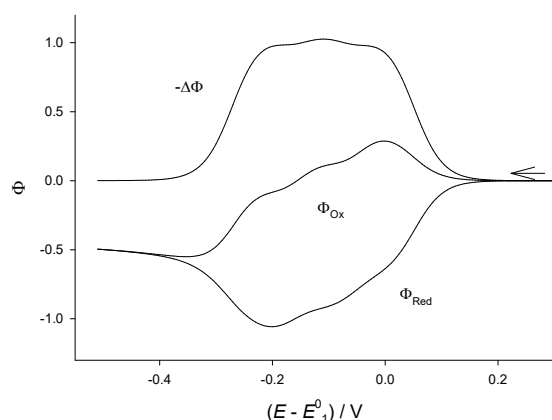


Figure 2. Dimensionless square wave voltammogram of reversible three step electrode reaction. $E_3 - E_1 = -0.22$ V, $E_2 - E_1 = -0.11$ V, $\rho = 0.1$, $E_{SW} = 50$ mV, $dE = -5$ mV and $E_{st} - E_1 = 0.25$ V.

to two electrons and occurs if $E_3 - E_2 \geq -0.1$ V. Its peak potential is equal to average value of the second and the third standard potentials. The third peak arises if $E_3 - E_2 < -0.1$ V.

The dependence of characteristic currents of reversible electrode reaction on the parameter ρ is shown in Figure 3. The net peak current is a linear function of this parameter: $-\Delta\Phi_p = 2.66\rho + 2.66$. The same result was obtained for the scanning in the anodic direction. Considering the definition of ρ , the real net peak current is a linear function of square root of frequency, with the intercept that corresponds to the steady-state contribution: $-\Delta\Phi_p\sqrt{f} = 2.66\sqrt{f} + 2.66\sqrt{D}/r_0$. If $D = 9 \times 10^{-6}$ cm² s⁻¹ and $r_0 = 10^{-3}$ cm, the first term of this equation is bigger than the second one if $f > 9$ s⁻¹. The minima and maxima of components satisfy the following equations: $\Phi_{Red,min} = -2.88\rho - 1.64$ and $\Phi_{Ox,max} = -0.13\rho + 1.03$. If $E_{st} - E_1 = -0.3$ V and $dE = 5$ mV, these relationships are slightly different: $\Phi_{Red,min} = -2.87\rho - 1.24$ and $\Phi_{Ox,max} = -0.11\rho + 1.41$. Finally, the calculations were performed for the single electron voltammograms ($E_2 - E_1 = -0.5$ V and $E_3 - E_1 = -0.5$ V) and the following results were obtained: $-\Delta\Phi_{p,1} = 0.75\rho + 0.75$, $\Phi_{Red,min,1} = -0.93\rho - 0.48$, and $\Phi_{Ox,max,1} = -0.08\rho + 0.27$. They are in agreement with the results of previous simulations.^[26,27]

Square wave voltammograms of electrode reactions that are controlled by the kinetics of one or more electron transfers depend on the kinetic parameters $\kappa_1 = k_1(Df)^{-1/2}$ and $\lambda_j = k_{s,j}r_0/D$ (where $j = 1, 2$ and 3) and the sphericity parameter ρ and the standard potentials of the three steps. The parameters κ_1 and ρ can be changed by the variation

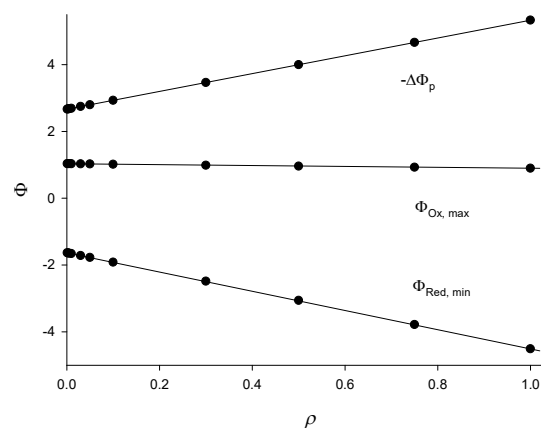


Figure 3. Dependence of dimensionless net peak current, the minimum of forward component and the maximum of backward component of square wave voltammogram of reversible three step electrode reaction on the sphericity parameter. $E_3 = E_2 = E_1$, $E_{SW} = 50$ mV, $dE = -5$ mV and $E_{st} - E_1 = 0.3$ V. The straight lines are linear approximations.

of frequency, but their ratio $\lambda_j = \kappa_j / \rho$ depends only on the characteristics of electrode and electroactive species. Figure 4 shows that a certain electrode reaction appears more irreversible if the radius of electrode is smaller. The net peak potential changes from -0.090 V to -0.155 V vs. E_1 if the radius is diminished from 10^{-2} cm to 10^{-3} cm. The calculations have shown that within this range the following linear relationship exists: $E_p - E_1 = 0.065 \log r_0 + 0.041$ V. If the radius is increased to 0.1 cm, the peak potential tends to -0.065 V, which is the value that is characteristic for planar electrode. The dimensionless net peak current is inversely proportional to the electrode radius: $-\Delta\Phi_p = 3.95 \times 10^{-4} r_0^{-1} + 0.63$. These show that in the simulations the parameters κ_1 , λ_j , and ρ can not be changed independently. Instead, the frequency has to be varied, for the constant values of electrode radius and the other reaction parameters. Furthermore, the scan direction is experimental variable.

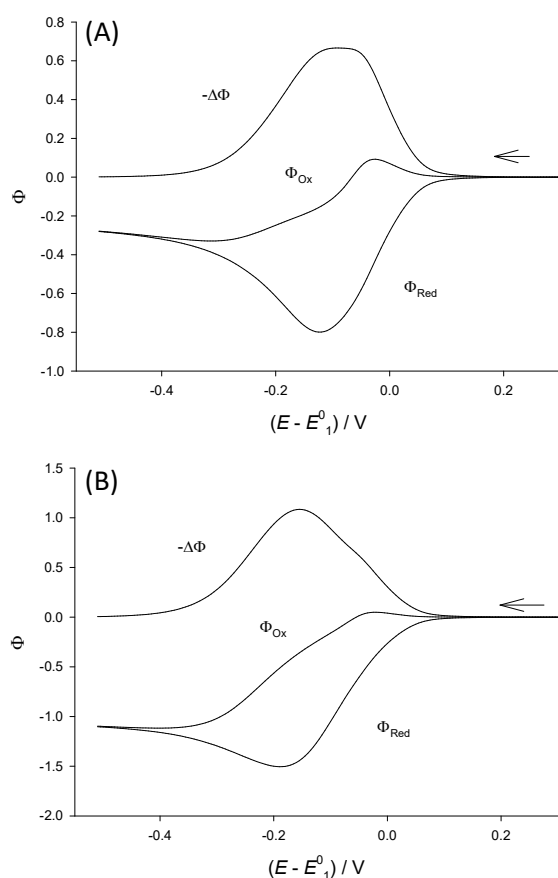


Figure 4. Dimensionless square wave voltammograms of three step electrode reaction. $E_3 = E_2 = E_1$, $D = 9 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, $f = 100 \text{ s}^{-1}$, $E_{SW} = 50 \text{ mV}$, $dE = -5 \text{ mV}$, $E_{st} - E_1 = 0.3 \text{ V}$, $k_{s_1} = 10^{-3} \text{ cm s}^{-1}$, $k_{s_2} = k_{s_3} = 1 \text{ cm s}^{-1}$, $\alpha_1 = \alpha_2 = \alpha_3 = 0.5$ and $r_0 = 10^{-2}$ cm (A) and 10^{-3} cm (B).

The voltammogram shown in Figure 4A is typical for electrode reaction in which the first electron transfer is the rate determining step. It consists of a single peak at all frequencies if the first transfer coefficient is bigger than 0.3. In the case of cathodic scan direction, the response may split in two peaks if $\alpha_1 = 0.25$. An example is shown in Figure 5. The second peak is caused mainly by the reduction component. The potential of minimum of this component is much lower than the potential of maximum of the oxidation component. The response with two peaks may also appear in the case of anodic scan direction. This can be seen in Figure 6. Again, the second peak is caused by the local minimum of reduction component. The oxidation component exhibits a shoulder at 0.015 V vs. E_1 that

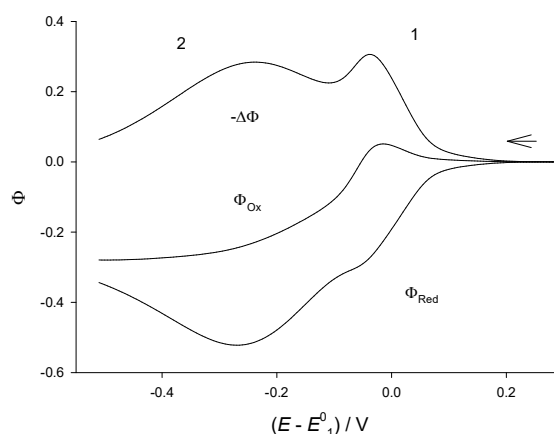


Figure 5. Dimensionless square wave voltammogram of three step electrode reaction; $\alpha_1 = 0.25$ and $r_0 = 10^{-2}$ cm. All other parameters are as in Figure 4.

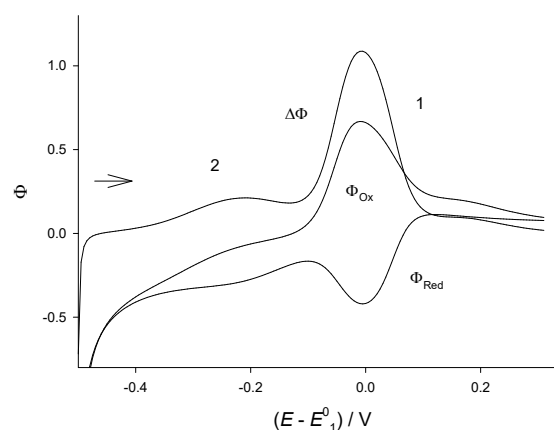


Figure 6. Dimensionless square wave voltammogram of three step electrode reaction. $E_{st} - E_1 = -0.5 \text{ V}$, $dE = 5 \text{ mV}$, $r_0 = 10^{-2}$ cm and $f = 10^3 \text{ s}^{-1}$. All other parameters are as in Figure 4.

corresponds to irreversible oxidation of the first intermediate. The first peak of the split response corresponds to the second and the third electron transfers that are fast and reversible. This peak is smaller in Figure 5 than in Figure 6. If the scan direction is cathodic, a small amount of the first intermediate that is created at -0.040 V vs. E_1 continues rapidly to be reduced to the final product and reoxidized back to Int_1 at -0.015 V. The massive reduction of the reactant that occurs at -0.270 V is totally irreversible and the backward component is also reductive current. This is because the product is stable at the potentials lower than -0.1 V vs. E_1 . Similar reasoning applies to the anodic scan direction. In the oxidation of product, the third step is the slowest one. The first peak appears at -0.005 V vs. E_1 and corresponds to the creation of the first intermediate and the small amount of the reactant. The latter is reduced back to Int_1 at -0.210 V vs. E_1 .

Figure 7 presents relationships between peak potentials and the logarithm of frequency. For the

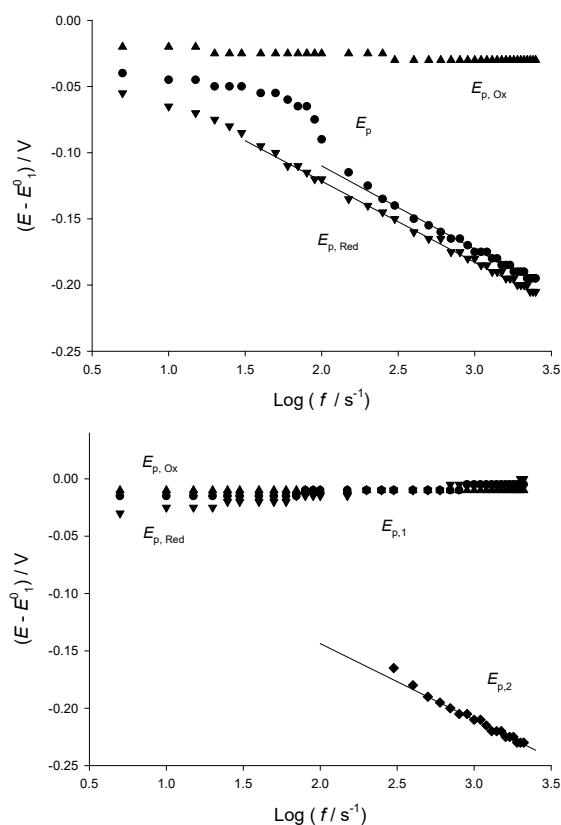


Figure 7. Dependence of peak potentials of square wave voltammograms of three step electrode reaction on the logarithm of frequency. $E_{\text{st}} - E_1 = 0.3 \text{ V}$ (A) and -0.5 V (B), $dE = -5 \text{ mV}$ (A) and 5 mV (B) and $r_0 = 10^{-2} \text{ cm}$. All other parameters are as in Figure 4. The straight lines are linear approximations.

cathodic scan direction and the frequency higher than 100 s^{-1} , the net peak potential and the potential of minimum of reduction component satisfy the following equations: $E_p - E_1 = -(RT/2\alpha_1 F) \log f + 0.016 \text{ V}$ and $E_{p, \text{Red}} - E_1 = -(RT/2\alpha_1 F) \log f + 0.001 \text{ V}$. For the anodic scan direction the potential of the first peak is independent of frequency, but the first transfer coefficient can be determined from the dependence of the second peak on the logarithm of frequency: $E_{p,2} - E_1 = -(RT/2\alpha_1 F) \log f - 0.011 \text{ V}$.

The standard potentials determine the stability of intermediates and the apparent reversibility of electrode reaction. If $E_2 - E_1 = 0.2 \text{ V}$, $E_3 = E_2$, $E_{\text{st}} - E_1 = 0.3 \text{ V}$, $dE = -5 \text{ mV}$, $r_0 = 10^{-2} \text{ cm}$ and all other parameters are as in Figure 4, the oxidation component is entirely negative at all frequencies (see Figure 8) and the net peak potential depends linearly on the logarithm of frequency if the frequency is higher than 20 s^{-1} . This is because the concentration of the first intermediate at the first standard potential is lower for $(E_1 + E_2 + E_3)/3 > E_1$ than for $(E_1 + E_2 + E_3)/3 = E_1$. The oxidation current of the first step depends on the concentration of the first intermediate, while the reduction current depends on the reactant concentration. This is the reason why the reaction appears more irreversible for $E_2 - E_1 = 0.2 \text{ V}$ and $E_3 = E_2$ than for $E_3 = E_2 = E_1$. If the scan direction is anodic and all other conditions are as above, the second peak is well developed at the frequency as low as 10 s^{-1} and the second peak potential is the linear function of the logarithm of frequency within the whole frequency range.

In the three step electrode reaction both the first and the second electron transfers can be slow. Figures 9 and 10 show a special case in which the second transfer coefficient is smaller than the first one, but the rate

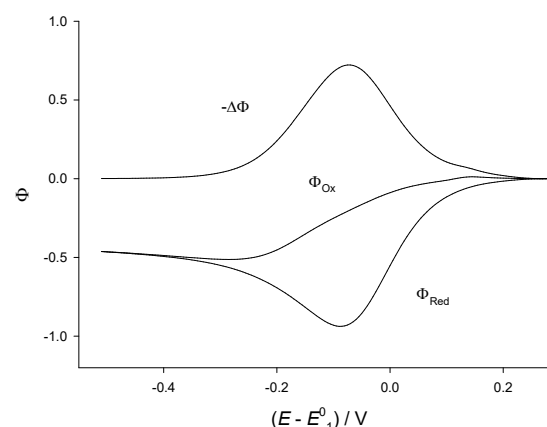


Figure 8. Dimensionless square wave voltammogram of three step electrode reaction. $E_2 - E_1 = 0.2 \text{ V}$, $E_3 = E_2$, $r_0 = 10^{-2} \text{ cm}$ and $f = 10 \text{ s}^{-1}$. All other parameters are as in Figure 4.

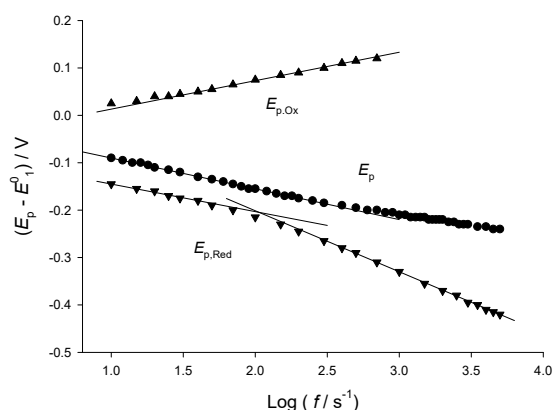


Figure 9. Dependence of peak potentials of square wave voltammogram of three step electrode reaction on the logarithm of frequency. $E_3 = E_2 = E_1$, $D = 9 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, $r_0 = 10^{-2} \text{ cm}$, $E_{SW} = 50 \text{ mV}$, $dE = -5 \text{ mV}$, $k_{s_1} = 10^{-3} \text{ cm s}^{-1}$, $k_{s_2} = 10^{-3} \text{ cm s}^{-1}$, $k_{s_3} = 1 \text{ cm s}^{-1}$, $\alpha_1 = 0.5$, $\alpha_2 = 0.25$ and $\alpha_3 = 0.5$. Straight lines are linear approximations.

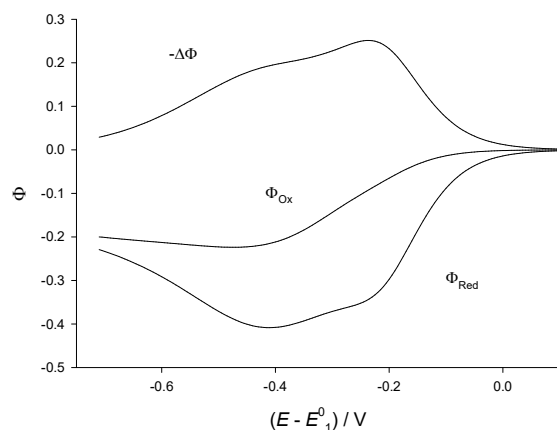


Figure 10. Dimensionless square wave voltammogram of three step electrode reaction. $E_{st} - E_1 = 0.1 \text{ V}$ and $f = 3000 \text{ s}^{-1}$. All other parameters are as in Figure 9.

constants of these two steps are equal. The relationships between peak potentials and the logarithm of frequency are linear for all values of this argument. The net response exhibits a single peak and its potential is defined by the equation: $E_p - E_1 = -(RT/2\alpha_1 F)\log f - 0.025 \text{ V}$ that applies for $f < 300 \text{ s}^{-1}$. At higher frequency the slope of this straight line changes to -0.047 V . This can be explained by the separation between the net peak and the minimum of the reduction component (see Figure 10). The potential of the latter satisfies two equations: $E_{p,Red} - E_1 = -(RT/2\alpha_1 F)\log f - 0.087 \text{ V}$ (if $f < 100 \text{ s}^{-1}$) and $E_{p,Red} - E_1 = -(RT/2\alpha_2 F)\log f + 0.056 \text{ V}$. The second

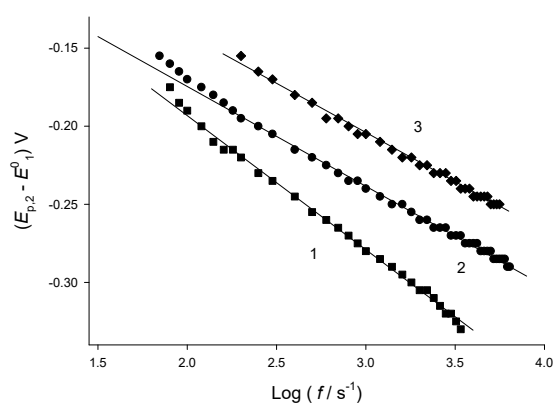


Figure 11. Dependence of the potential of the second peak on the logarithm of frequency. $E_{st} - E_1 = -0.6 \text{ V}$, $dE = 5 \text{ mV}$ and $\alpha_2 = 0.25$ (1), 0.5 (2) and 0.75 (3). All other parameters are as in Figure 9. Straight lines are linear approximations.

equation enables the determination of the second transfer coefficient. The potential of maximum of oxidation component depends on the first transfer coefficient: $E_{p,Ox} - E_1 = [RT/2(1-\alpha_1)F]\log f - 0.047 \text{ V}$. The net response develops a shoulder at the highest frequencies and the potential of its peak under these conditions is not suitable for the determination of transfer coefficients. The described phenomenon vanishes if $\alpha_1 = 0.5$ and $\alpha_2 \geq 0.4$. For equal transfer coefficients a single slope $\Delta(E_p - E_1)/\Delta\log f = -RT/2\alpha_1 F$ appears for all frequencies.

The variation of scan direction is not useful for the estimation of the second transfer coefficient. For the conditions reported in Figure 9 the response consists of a reversible peak at -0.005 V vs. E_1 and totally irreversible peak that depends linearly on the logarithm of frequency: $E_{p,2} - E_1 = -0.086\log f - 0.022 \text{ V}$. This straight line is shown in Figure 11. From the slope -0.086 V the transfer coefficient $\alpha = 0.34$ can be calculated, which is neither α_1 , nor α_2 . The slopes of the second and the third straight lines in Figure 11 are mutually equal: $\Delta(E_{p,2} - E_1)/\Delta\log f = -RT/2\alpha_1 F$.

Finally, the possibility that all three electron transfers are equally slow was investigated. The value of rate constants that is characteristic for quasireversible electrode reactions was chosen. The results are shown in Figure 12. The relationships between peak potentials and the logarithm of frequency are curves that approach asymptotes at the highest frequencies. For the cathodic scan direction these straight lines are as follows: $E_p - E_1 = -0.057\log f + 0.081 \text{ V}$, $E_{p,Red} - E_1 = -0.056\log f + 0.068 \text{ V}$, and $E_{p,Ox} - E_1 = 0.042\log f - 0.097 \text{ V}$, while for the anodic scan direction they are: $E_{p,1} - E_1 = 0.078\log f - 0.164 \text{ V}$ and $E_{p,2} - E_1 = -0.108\log f + 0.215 \text{ V}$.

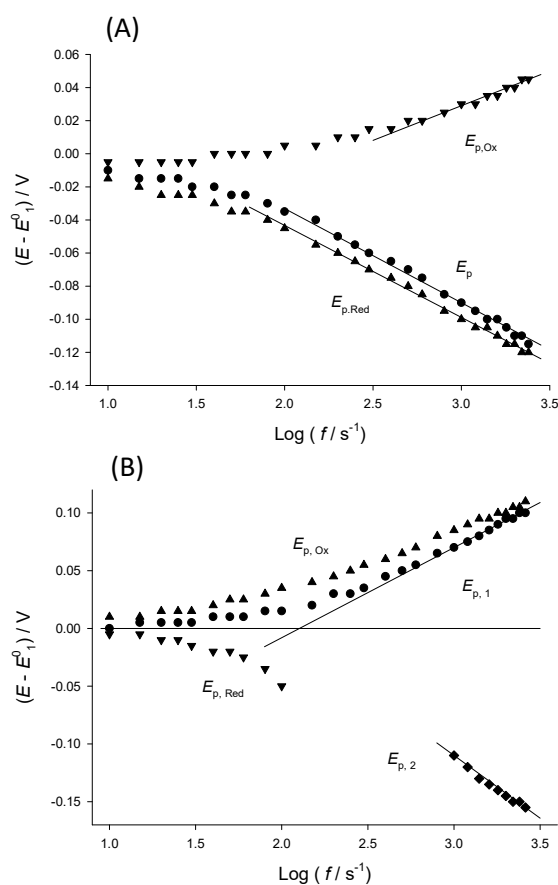


Figure 12. Dependence of peak potentials on the logarithm of frequency; $k_{s_1} = k_{s_2} = k_{s_3} = 10^{-2} \text{ cm s}^{-1}$, $\alpha_1 = \alpha_2 = \alpha_3 = 0.5$ and $E_{st} - E_1 = 0.2 \text{ V}$ and $dE = -5 \text{ mV}$ (A) and $E_{st} - E_1 = -0.4 \text{ V}$ and $dE = 5 \text{ mV}$ (B). All other parameters are as in Figure 9. Straight lines are linear approximations.

The slopes -0.057 V and -0.056 V can be used for the estimation of an average transfer coefficient, but the slope of the oxidation component is too low because this component gradually vanishes as the frequency is increased. The slopes in Figure 12B are too high and indicate apparent transfer coefficients that are smaller than the value used in the calculations. This confirms that the anodic scan direction may be inapt for the transfer coefficients determination. However, the intersections of straight lines in Figure 12B and the line $E = E_1$ correspond to the logarithms of the critical frequency $\log f_{crit} = 2.1$ and $\log f_{crit} = 2.0$ that are close to the negative value of the logarithm of the average rate constant: $\log f_{crit} \approx -\log k_s$.

CONCLUSION

In square wave voltammetry the scan direction can be either cathodic or anodic. If the response of three step electrode reaction does not depend on the scan direction,

that reaction is reversible for the applied frequency. The peak current depends linearly on the square root of frequency regardless of the number of peaks in the response. As the frequency tends to zero, the current tends to some finite value, which is called the steady-state contribution.

Reactions that are controlled by the kinetics of electron transfer may appear less reversible on the electrode with smaller radius. The responses to various frequencies can be compared to each other only if they are recorded on the electrodes with the same radius. Besides, the responses of kinetically controlled reactions depend on the scan direction. In the case that the first electron transfer is the rate determining step and that the scan direction is cathodic, the net response consists of a single peak at all frequencies if $\alpha_1 > 0.3$. If this condition is not satisfied, the response may split in two peaks. The response of this reaction recorded by using the anodic scan direction exhibits either one, reversible peak at low frequency, or the first, reversible and the second, totally irreversible peaks at the highest frequency. The transfer coefficient of the first electron transfer can be determined from the slope of the dependence of the net peak current on the logarithm of frequency. The kinetics of electron transfer is a function of the rate constant and of the stability of the first intermediate. So, the rate constant cannot be estimated if the standard potentials are not known. If both the first and the second electron transfers are equally slow, the second transfer coefficient can be measured only if it is smaller than the first one. The difference between responses recorded with two scan directions indicates that more than one electron is transferred in the electrode reaction. If the first peak potential of the voltammogram recorded with the anodic scan direction depends on frequency, then all electron transfers are kinetically controlled.

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