Tafel Plot of an EE Mechanism

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Abstract: A model of linear scan voltammetry of the EE mechanism consisting of the kinetically controlled single electron transfer followed by the reversible transfer of the second electron is developed. The Tafel plot of this mechanism is linear if the intermediate is either very stable or highly unstable. If the first electrode reaction is irreversible and these conditions are satisfied, the slope of Tafel plot is proportional to the transfer coefficient of the first electron.

Keywords: transfer coefficient, linear scan voltammetry, simulation, Tafel plot, EE mechanism.

INTRODUCTION

THERE are opinions that a concerted transfer of two electrons is highly improbable and that each transfer must occur independently.[1–3] Electrode reactions involving two electrons are common.[4–6] Depending on the stability of intermediate, either one or two peaks may appear in a voltammetry.[7–10] This is called EE mechanism.[11,12] If the electrons are exchanged one after another, at different potentials, it is obvious that each reaction has its own kinetic parameters, but if the intermediate is unstable, so that both electrons are transferred simultaneously, then the second transfer may influence the kinetics of the first one.[13,14] In this communication the determination of the transfer coefficient of the first electron of an EE mechanism is described as it depends on the standard potential of the second electron.

THE MODEL

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

$$\text{Ox}^{(m+2)+} + \text{e}^- \leftrightarrow \text{Int}^{(m+1)+} \tag{1}$$

$$\text{Int}^{(m+1)+} + \text{e}^- \leftrightarrow \text{Red}^{m+} \tag{2}$$

It is assumed that the first electron transfer is kinetically controlled while the second one is fast and reversible. Furthermore, it is assumed that all electroactive species have equal diffusion coefficients. For the mass transfer realized by the planar, semi-infinite diffusion, the following system of differential equations has to be solved:

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

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

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

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

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

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

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

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

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

$$(c_{Int})_{x=0} = (c_{Red})_{x=0}\, e^{\varphi_2} \qquad (12)$$

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

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

The meanings of all symbols are reported in the Table 1. Differential equations [Eq. (3)] − [Eq. (5)] are solved by Laplace transforms and the method of numerical integration.[15,16] The solution is the system of recursive formulae for the dimensionless currents $\Phi_j = I_j (FSc_{Ox}^*)^{-1}[DFv/RT]^{-0.5}$, where $j = 1$ and 2 and $\Phi = \Phi_1 + \Phi_2$. The response is calculated for the linear scan voltammetry.

$$\Phi_{1,p} = N^{-1}\left[-\lambda e^{-\alpha_1\varphi_{1,p}} + WZ\sum_{j=1}^{p-1}\Phi_{1,j}s_{p-j+1}\right] \qquad (15)$$

$$\Phi_{2,p} = (1 + e^{\varphi_{2,p}})^{-1}\sum_{j=1}^{p}\Phi_{1,j}s_{p-j+1} - \sum_{j=1}^{p-1}\Phi_{2,j}s_{p-j+1} \qquad (16)$$

$$N = 1 + W(1 + e^{\varphi_{2,p}}(1 + e^{\varphi_{1,p}}))(1 + e^{\varphi_{2,p}})^{-1} \qquad (17)$$

$$W = 2b\lambda e^{-\alpha_1\varphi_{1,p}} \qquad (18)$$

$$Z = e^{\varphi_{1,p}}(1 + e^{\varphi_{2,p}})^{-1} - 1 - e^{\varphi_{1,p}} \qquad (19)$$

$$\lambda = k_{s,1}\left(\frac{DFv}{RT}\right)^{-0.5} \qquad (20)$$

$$v = \frac{dE}{dt} \qquad (21)$$

$$b = \sqrt{\frac{FdE}{\pi RT}} \qquad (22)$$

$$s_q = \sqrt{q} - \sqrt{q-1} \qquad (23)$$

The potential increment $dE = 10^{-4}$ V is used.

RESULTS AND DISCUSSION

A linear scan voltammetric response of the EE mechanism (1) and (2) depends on the thermodynamic stability of the intermediate and on the kinetics of the first electrode reaction. If $E_2^\circ - E_1^\circ = -0.3$ V and $\lambda \geq 100$ the voltammogram exhibits the minima at −0.029 V and −0.327 V *vs.* E_1°. Their dimensionless peak currents are equal to −0.446 and

Table 1. Meaning of symbols.

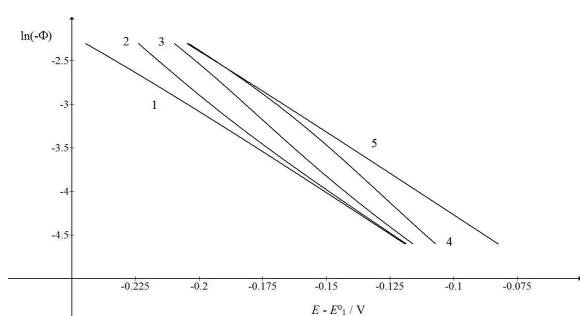| Symbol	Meaning	Symbol	Meaning
α_1	transfer coefficient of the first step	c_y	concentrations of electroactive species
c_{Ox}^*	bulk concentration of the reactant	D	common diffusion coefficient
E	potential	E°	standard potential
F	Faraday constant	I	current
$k_{s,i}$	standard rate constant	λ	dimensionless rate constant
R	gas constant	S	electrode surface area
T	temperature	t	time
v	scan rate	x	distance
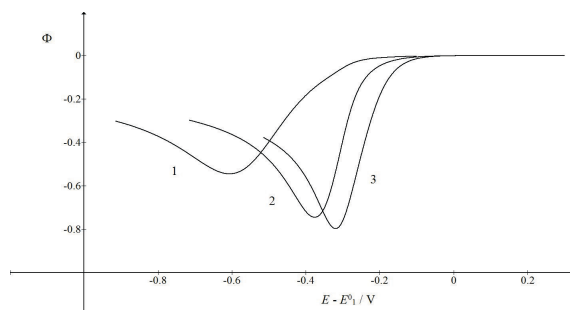
Figure 1. Dimensionless voltammograms of the EE mechanism; $E_2^\circ - E_1^\circ = -0.3$ V, $\lambda = 10^{-3}$ and $\alpha_1 = 0.3$ (1), 0.5 (2) and 0.7 (3).

−0.606, respectively. It is an example of two fast and reversible electron transfers with stable intermediate. Note that the dimensionless kinetic parameter $\lambda = 100$ corresponds to the standard rate constant $k_{s,1}$ 0.6 cm s^{-1} if $D = 10^{-5}$ cm^2 s^{-1} and the scan rate is 0.1 V s^{-1}. By decreasing the dimensionless kinetic parameter λ to 1 and 0.1, the peak currents and peak potentials change to $\Phi_{p,1} = -0.407$, $E_{p,1} = -0.051$ V, $\Phi_{p,2} = -0.612$ and $E_{p,2} = -0.327$ V and to $\Phi_{p,1} = -0.358$, $E_{p,1} = -0.143$ V, $\Phi_{p,2} = -0.641$ and $E_{p,2} = -0.325$ V, respectively. If $\lambda = 0.01$ these two minima merge into a single peak at −0.324 V. Three examples of such response are shown in Fig. 1 for three values of the transfer coefficient. If $\alpha_1 = 0.5$ the peak current is −0.745 and the peak potential is −0.376 V *vs.* E_1°. For $\alpha_1 = 0.3$ and $\alpha_1 = 0.7$ the minima appear at −0.607 V and −0.319 V and the peak currents are −0.545 and −0.797, respectively. If $\lambda \geq 10^{-4}$ and $E_2^\circ - E_1^\circ = -0.3$ V, the peak current becomes independent of λ but the peak potential depends linearly on the logarithm of this parameter: $E_p = E_1^\circ + 2.303(RT/\alpha_1 F)\log\lambda - 0.0214$ V.

Fig. 2 shows the influence of the standard potential of the second electron transfer on the voltammogram of EE mechanism that is characterized by the irreversible transfer of the first electron. If $E_2^\circ - E_1^\circ = -0.5$ V the minima are
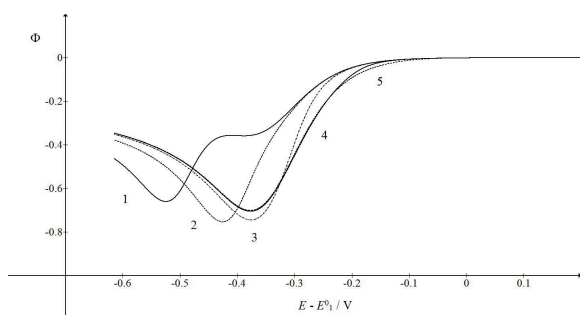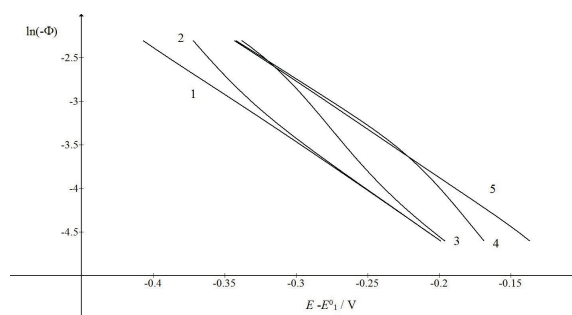
Figure 2. Voltammograms of the EE mechanism; $\lambda = 10^{-3}$, $\alpha_1 = 0.5$ and $E_2^\circ - E_1^\circ$ / V = −0.5 (1), −0.4 (2), −0.3 (3), −0.2 (4) and −0.1 (5).

Figure 4. Tafel plot of the EE mechanism; $\lambda = 10^{-3}$, $\alpha_1 = 0.3$ and $E_2^\circ - E_1^\circ$ / V = −0.5 (1), −0.4 (2), −0.3 (3), −0.2 (4) and −0.1 (5).
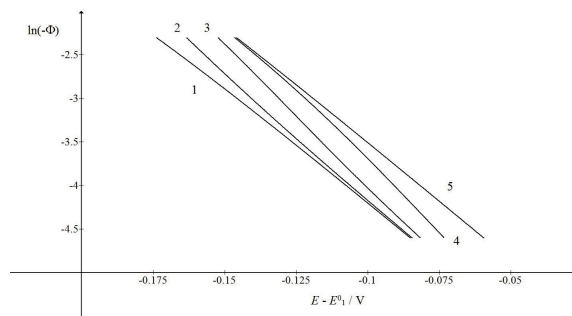

Figure 3. Dependence of natural logarithm of negative current of the EE mechanism on the electrode potential; $\lambda = 10^{-3}$, $\alpha_1 = 0.5$ and $E_2^\circ - E_1^\circ$ / V = −0.4 (1), −0.25 (2), −0.2 (3), −0.15 (4) and 0.0 (5).


Figure 5. Tafel plot of the EE mechanism; $\lambda = 10^{-3}$, $\alpha_1 = 0.7$ and $E_2^\circ - E_1^\circ$ / V = −0.4 (1), −0.2 (2), −0.15 (3), −0.1 (4) and 0.0 (5).

separated, but they are merged if $E_2^\circ - E_1^\circ \geq$ −0.4 V. The difference between standard potentials that is higher than −0.1 V has no influence on the voltammograms.

The transfer coefficient of the irreversible electrode reaction can be determined by the Tafel plot.[2] The method is developed for a single electron reaction and here we are applying it to the current of the EE mechanism. This current is a sum of two components originating from the first and the second electron transfers. The second component depends on the standard potential of the second reaction. Fig. 2 shows that two components can be either separated or the second one can be hidden by the first component. The Tafel plot of the EE mechanism is the relationship between the natural logarithm of the negative value of the EE current and the electrode potential. Fig. 3 shows these relationships calculated for the voltammograms that are shown in Fig. 2. The logarithms are calculated for the lower 15 % of currents (0.01 < $-\Phi$ < 0.1). The plots are linear if $E_2^\circ - E_1^\circ$ is either lower than −0.4 V or higher than zero. The slopes of these straight lines are equal to −19 V^{-1} and, considering that $F/RT = 38.92$ V^{-1}, they correspond to $\alpha_1 = 0.49$. If the second standard potential lies within this interval, the Tafel plot of EE mechanism is a curve with two asymptotes. Similar plots were obtained for

$\alpha_1 = 0.3$ and $\alpha_1 = 0.7$. They are shown in Fig. 4 and Fig. 5.

The slopes of straight lines in Fig. 4 and Fig. 5 are −11 V^{-1} and −26 V^{-1} and they correspond to $\alpha_1 = 0.28$ and $\alpha_1 = 0.67$, respectively. The limits of $E_2^\circ - E_1^\circ$ are lower for $\alpha_1 = 0.3$ than for $\alpha_1 = 0.7$. Besides, these limits depend on λ value, being lower for smaller λ. For instance, if $\alpha_1 = 0.5$ and $\lambda = 10^{-2}$ the limits are −0.3 V and 0.2 V, but if $\alpha_1 = 0.5$ and $\lambda = 10^{-4}$ they are −0.5 V and −0.1 V. The left limit is connected to the separation of minima. If $E_2^\circ - E_1^\circ =$ −0.3 V, $\alpha_1 = 0.5$ and $\lambda = 0.1$ the voltammogram is similar to the curve 1 in the Fig. 2. The right limit can be explained by the analysis of current components that are shown in Fig. 6.

If $E_2^\circ - E_1^\circ =$ −0.4 V (Fig. 6A) the second component is negligible in the potential range of Tafel analysis and the EE current is equal to the first component: ln(−Φ) = ln(−Φ_1). If $E_2^\circ = E_1^\circ$ the components are equal and the EE current is twice as big as the first component: $\Phi = 2\Phi_1$ and ln(−Φ) = ln(−Φ_1) + ln(2). This means that the asymptotes in Figures 3, 4 and 5 are vertically separated for ln(2) = 0.693. For instance, the straight lines 1 and 5 in Fig. 3 are defined by ln $(-\Phi)_{E-E_1^\circ=-0.2 V}$ = −3.085 and −2.38, which is a difference of 0.705. Considering [Eq. (16)], the current Φ_2 is defined by Φ_1 and the term [1 + exp(φ_2)$^{-1}$]. The condition $\Phi_2 \ll \Phi_1$ that can be seen in Fig. 6A can be satisfied if exp(φ_2) ≥ 10^3. For
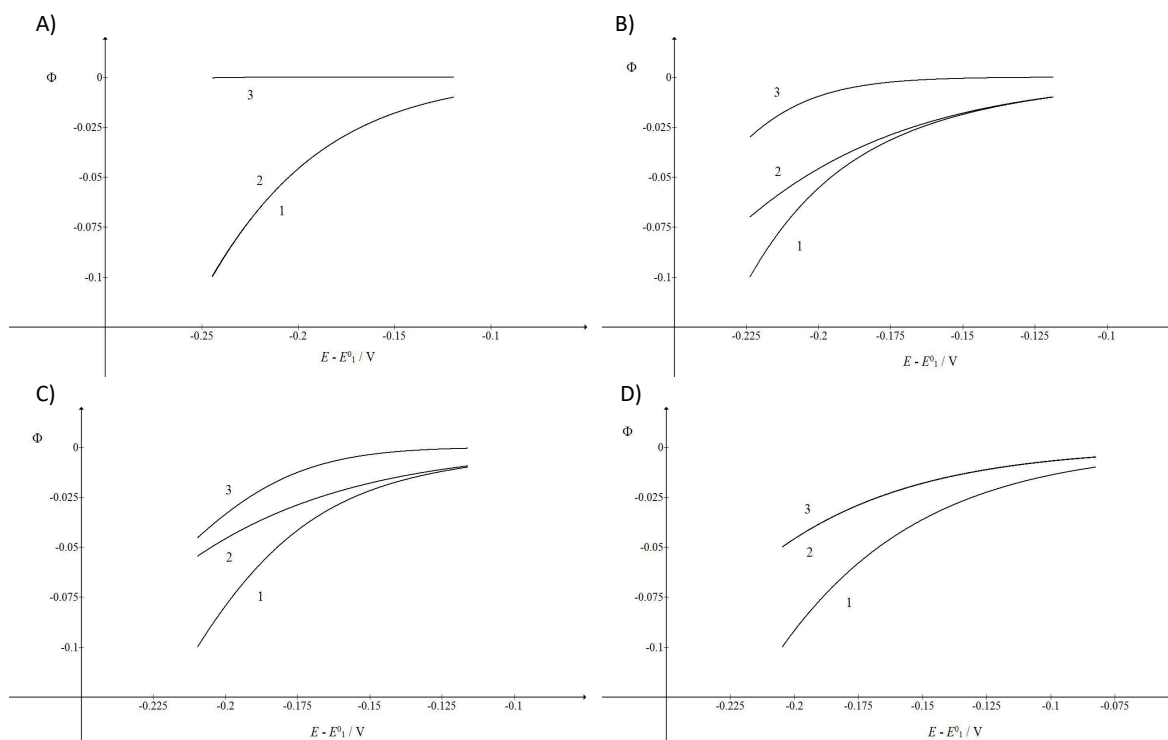
Figure 6. The current of EE mechanism (1) and its first (2) and the second (3) components; $\lambda = 10^{-3}$, $\alpha_1 = 0.5$ and $E_2^{\circ} - E_1^{\circ}$ / V = −0.4 (A), −0.25 (B), −0.2 (C) and 0.0 (D).

$E_2^{\circ} - E_1^{\circ} = -0.2$ V, which is the potential from the Tafel range, this condition is: $\exp[F(-0.2 - E_2^{\circ}) / RT] \geq 10^3$ and the result is $E_2^{\circ} \leq -0.377$ V. This is the condition for the left asymptote. In the same way the condition $\Phi_2 = \Phi_1$ can be achieved if $\exp(\varphi_2) \leq 10^{-3}$. At the same potential as above, the result is $E_2^{\circ} \geq -0.023$ V. This is the condition for the right asymptote. However, this reasoning relies on the simulation of the EE response, which is needed to determine the potential range of Tafel analysis that depends on $\alpha_1 =$ and λ parameters. Qualitatively, the second condition is satisfied if the response exhibits a single minimum, if the Tafel plot is linear and if the value of the transfer coefficient calculated from its gradient is equal to the value of α that is calculated from the dependence of peak potential on the logarithm of scan rate.

CONCLUSION

The Tafel plot of EE mechanism consisting of irreversible and reversible electron transfers is a curve with two asymptotes. The slopes of these straight lines are equal to $-\alpha_1 F/RT$, where α_1 is the transfer coefficient of the first electron. The left asymptote appears if the standard potential of the second electron is much lower (for the reduction) than the standard potential of the first electron, so that the voltammogram exhibits two, well separated minima. The right asymptote corresponds to highly unstable intermediate, so that the transfer of the second electron follows the first one immediately.

REFERENCES

[1] C. Batchelor-McAuley, E. Kätelhön, E. O. Barnes, R. G. Compton, E. Laborda, A. Molina, *ChemistryOpen* **2015**, *4*, 224–260. https://doi.org/10.1002/open.201500042

[2] R. Guidelli, R. G. Compton, J. M. Feliu, E. Gileadi, J. Lipkowski, W. Schmickler, S. Trasatti, *Pure Appl. Chem.* **2014**, *86*, 245–258. https://doi.org/10.1515/pac-2014-5026

[3] C. Batchelor-McAuley, R. G. Compton, *J. Electroanal. Chem.* **2012**, *669*, 73–81. https://doi.org/10.1016/j.jelechem.2012.01.016

[4] D. H. Evans, *Chem. Rev.* **2008**, *108*, 2113–2144. https://doi.org/10.1021/cr068066l

[5] D. H. Evans, M. W. Lehmann, *Acta Chem. Scand.* **1999**, *53*, 765–774.

[6] N. A. Macias-Ruvalcaba, D. H. Evans, *J. Phys. Chem. B* **2005**, *109*, 14642–14647. https://doi.org/10.1021/jp051641p

[7] F. Barriere, W. E. Geiger, *J. Am. Chem. Soc.* **2006**, *128*, 3980–3989.

https://doi.org/10.1021/ja058171x

[8] M. Quan, D. Sanchez, M. F. Wasylkiw, D. K. Smith, *J. Am. Chem. Soc*. **2007**, *129*, 12847–12856. https://doi.org/10.1021/ja0743083

[9] C. Batchelor-McAuley, Q. Li, S. M. Dapin, R. G. Compton, *J. Phys. Chem. B* **2010**, *114*, 4094–4100. https://doi.org/10.1021/jp1008187

[10] E. Laborda, A. Molina, Q. Li, C. Batchelor-McAuley, R. G. Compton, *Phys. Chem. Chem. Phys*. **2012**, *14*, 8319–8327. https://doi.org/10.1039/C2CP40265C

[11] M. Sakai, N. Ohnaka, *J. Electrochem. Soc*. **1990**, *137*, 576–582. https://doi.org/10.1149/1.2086509

[12] A. Molina, C. Serna, M. Lopez-Tenes, M. M. Moreno, *J. Electroanal. Chem*. **2005**, *576*, 9–19. https://doi.org/10.1016/j.jelechem.2004.09.027

[13] M. Lovrić, Š. Komorsky-Lovrić, *Croat. Chem. Acta* **2012**, *85*, 569–575. https://doi.org/10.5562/cca2126

[14] Š. Komorsky-Lovrić, M. Lovrić, *Int. J. Electrochem. Sci*. **2014**, *9*, 435–444. www.electrochemsci.org/papers/vol9/90100435.pdf

[15] M. Lovrić, *Croat. Chem. Acta* **2022**, *95*, 111–115. https://doi.org/10.5562/cca3965

[16] Bieniasz LK, Modelling electrochemical experiments by the integral equation method, Springer, Berlin, **2015**. https://doi.org/10.1007/978-3-662-44882-3

DOI: 10.5562/cca4035

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