Theory of square-wave voltammogram starting at the equilibrium potential

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ABSTRACT

If both a reactant and product of an electrode reaction are present in the bulk of solution, the square-wave voltammogram can be recorded by starting at the equilibrium potential. If the reaction is reversible, the redox state of investigated substance can be estimated from the ratio of peak currents of the forward and backward components. The degree of reversibility of the reaction can be assessed from the current at the starting potential. Also, the dependence of the logarithm of forward component of irreversible response on the electrode potential can be used for the calculation of transfer coefficient.

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1. Introduction

Square-wave voltammetry (SWV) has found wide application in electroanalysis and in the investigation of mechanisms and kinetics of electrode reactions [1–4]. In analysis, only the reactant is originally present in the solution [5–8], but for kinetic measurements both the reactant and product may exist initially [9–15]. In the first case, the excitating signal usually starts at the potential at which the reactant is stable at electrode surface, so that the current is zero at the beginning of measurement [1–8], although the reverse scan can be also used [16–21], particularly in stripping techniques [1,22–26]. In the second case the initial current is not zero regardless of starting potential [27] except if this potential is the equilibrium one [28,29]. However, in SWV the properties of responses that are recorded by starting at the equilibrium potential are not well known [1,4,6,8]. Here, the results of theoretical investigation of these voltammograms are described.

2. The model

A simple electron transfer reaction on the stationary, planar electrode is considered:

$$Ox^{m+} + ne^- \leftrightarrow Red^{(m-n)+} \tag{1}$$

It is assumed that both the reactant Ox^{m+} and the product $Red^{(m-n)+}$ are soluble in the aqueous electrolyte and are not adsorbed on the electrode surface. The mass transport is described by the following differential equations and boundary conditions:

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

$$\frac{\partial C_{Red}}{\partial t} = D \frac{\partial^2 C_{Red}}{\partial x^2} \tag{3}$$

$$t = 0, \quad x \geq 0 : \quad C_{Ox} = C_{Ox}^*, \quad C_{Red} = C_{Red}^* \tag{4}$$

$$t > 0, \quad x \to \infty : \quad C_{Ox} \to C_{Ox}^*, \quad C_{Red} \to C_{Red}^* \tag{5}$$

$$x = 0 : \quad D\left(\frac{\partial C_{Ox}}{\partial x}\right)_{x=0} = -\frac{I}{nFS} \tag{6}$$

$$D\left(\frac{\partial C_{Red}}{\partial x}\right)_{x=0} = \frac{I}{nFS} \tag{7}$$

For the fast and reversible electrode reaction the Nernst equation applies:

$$(C_{Ox})_{x=0} = (C_{Red})_{x=0} \exp(\varphi) \tag{8}$$

$$\varphi = \frac{nF}{RT}(E - E^0) \tag{9}$$

For kinetically controlled reaction the conditions at the electrode surface are defined by the Butler–Volmer equations:

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$$\frac{I}{nFS} = -K_s \exp(-\alpha\varphi)[(C_{Ox})_{x=0} - (C_{Red})_{x=0} \exp(\varphi)] \qquad (10)$$

The meanings of all symbols are listed in Table 1. Eqs. (2)–(10) are solved by digital simulation, using one thousand space increments and the time increment defined as: $\Delta t = \tau/25$ where $\tau = 1/2f$ (i.e. each square-wave half-period is divided into 25 time increments). The dimensionless diffusion coefficient $D\Delta t/\Delta x^2 = 0.4$ (in order to obtain stable and accurate results [30]) and the dimensionless kinetic parameter $k = k_s(Df)^{-1/2}$ were used. The scan starts at the equilibrium potential:

$$E_{eq} = E^0 + \frac{RT}{nF} \ln \frac{C_{Ox}^*}{C_{Red}^*} \qquad (11)$$

The result of simulation is the dimensionless current:

$$\Phi = \frac{I}{nFS(C_{Ox}^* + C_{Red}^*)\sqrt{Df}} \qquad (12)$$

In SWV the current is measured at the end of each pulse and the difference between the currents measured on two successive pulses is recorded as a net response ($\Delta\Phi = \Phi_f - \Phi_b$) and plotted as a function of the corresponding potential of the staircase waveform [1]. The forward and backward components of the response are also displayed.

3. Results and discussion

Fig. 1A shows theoretical square-wave voltammograms of reversible electrode reaction simulated for equal concentrations of reactant and product in the bulk of solution. The starting potential is equal to the standard potential. If the scan direction is negative, the forward current is reductive and the net response is negative. The minima of these two currents and the corresponding peak potentials are the following: $\Phi_{p,f} = -0.3748$, $E_{p,f} = -0.008$ V vs. E^0, $\Delta\Phi_p = -0.73405$ and $E_p = -0.003$ V. The backward component is in maximum at the starting potential. For the positive scan direction the response is centrosymmetric: $\Phi_{p,f} = 0.3748$, $E_{p,f} = 0.008$ V, $\Delta\Phi_p = 0.73405$ and $E_p = 0.003$ V. Also, the minimum of backward, reductive component appears at the start. The combination of positive and negative scans gives the oxidative and reductive components that resemble the components of the re-
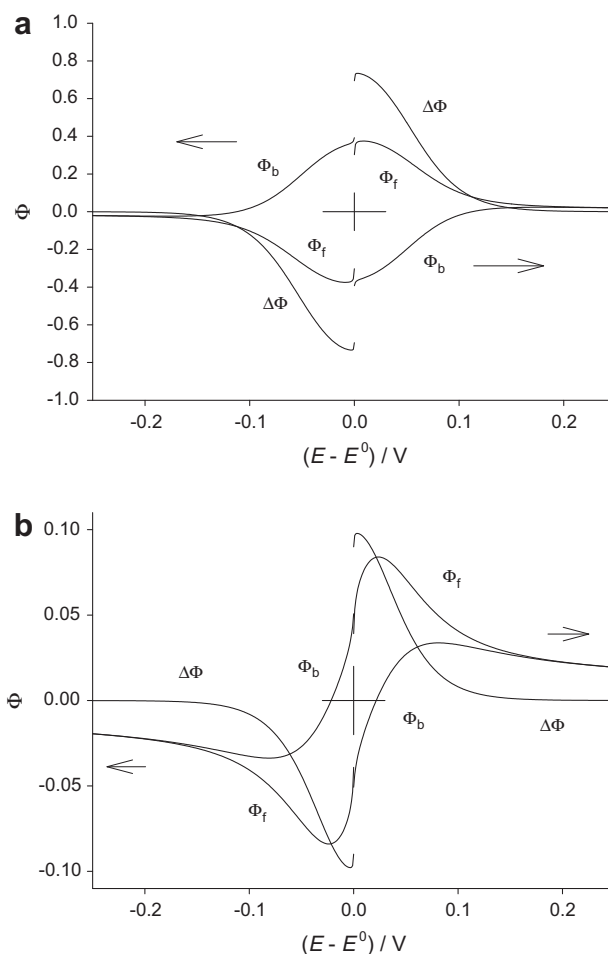

Fig. 1. Square-wave voltammograms (SWV) of reversible electrode reaction recorded by starting at the equilibrium potential. The scan direction is either positive ($dE = 0.001$ V), or negative ($dE = -0.001$ V). The net current ($\Delta\Phi = \Phi_f - \Phi_b$) and its forward ($\Phi_f$) and backward ($\Phi_b$) components are shown. $C_{Ox}^* = C_{Red}^*$, $n = 1$, $E_{eq} - E^0 = 0$ V and $E_{SW}/V = 0.050$ (a) and 0.005 (b).

sponses that start either at -0.3 V vs. E^0, or at 0.3 V vs. E^0. This is the consequence of superposition principle, which postulates that the concentrations of reactant and product of simple, reversible reaction at the electrode surface depend only on the potential, and not on the hydrodynamic conditions in the solution [31].

The influence of square-wave amplitude on net peak currents is shown in Table 2, for $C_{Ox}^* = C_{Red}^*$. These relationships are in agreement with the general theory of SWV [1], which means that this property does not depend on the starting potential. The amplitude influences the backward component primarily, as can be seen in Fig. 1B. For the positive scan direction and $E_{SW} = 0.005$ V, this com-

Table 1
List of symbols.

α	Transfer coefficient for the reduction
C_{Ox}	Reactant concentration
C_{Ox}^*	Bulk concentration of the reactant
C_{Red}	Product concentration
C_{Red}^*	Bulk concentration of the product
D	Common diffusion coefficient
dE	Scan increment
E	Electrode potential
E^0	Standard potential
E_{sw}	Square-wave amplitude
E_{eq}	Equilibrium potential
E_p	Peak potential
f	Square-wave frequency
F	Faraday constant
Φ	Dimensionless current
$\Delta\Phi_p$	Dimensionless net peak current
I	Current
k_s	Standard rate constant
$k = k_s(Df)^{-1/2}$	Dimensionless kinetic parameter
n	Number of electrons
R	gas constant
S	Electrode surface area
T	Absolute temperature
t	Time
x	Distance perpendicular to the electrode surface

Table 2
Influence of square-wave amplitude on the dimensionless net peak currents of reversible electrode reactions for $C_{Ox}^* = C_{Red}^*$ and $dE = \pm 0.001$ V.

E_{SW} (mV)	$\Delta\Phi_{p,red}$	$\Delta\Phi_{p,Ox}$
5	−0.09778	0.09778
10	−0.19052	0.19052
15	−0.27985	0.27985
20	−0.36440	0.36440
30	−0.51510	0.51510
40	−0.63826	0.63826
50	−0.73405	0.73405
60	−0.80575	0.80575
70	−0.85789	0.85789

ponent is reductive only for $E - E^0 < 0.022$ V, so that the net response is smaller than the forward component at all other potentials. However, the net peak potentials are independent of square-wave amplitude.

The voltammograms calculated for various concentrations of reactant and product of reversible electrode reaction are shown in Fig. 2. If $C_{Ox}^*/C_{Red}^* = 2$ the equilibrium potential is 0.0178 V *vs.* E^0, and if $C_{Ox}^*/C_{Red}^* = 0.5$ it is −0.0178 V. In both cases the response to the reductive scan is not a camera obscura image of the response caused by the oxidative scan. However, there is a central symmetry between Fig. 2A and B because of inverse concentration ratios. In the first figure the net response to the negative scan is absolutely bigger ($\Delta\Phi_p = -0.7364$ and $E_p - E^0 = -0.0002$ V) than the net response to the positive scan ($\Delta\Phi_p = 0.6849$ and $E_p - E^0 = 0.0198$ V). Furthermore, both forward and backward components that correspond to the reductive scan exhibit well defined extremes ($\Phi_{p,f} = -0.3981$, $E_{p,f} = -0.0022$ V, $\Phi_{p,b} = 0.3389$ and $E_{p,b} = 0.0018$ V), while the minimum of the backward component of the response to the oxidative scan appears at the starting potential. In Fig. 2B these relationships are opposite because $C_{Red}^* > C_{Ox}^*$. The response to the oxidative scan consists of well developed components ($\Phi_{p,f} = 0.3981$, $E_{p,f} = 0.0022$ V, $\Phi_{p,b} = -0.3389$ and $E_{p,b} = -0.0018$ V) and its net peak current ($\Delta\Phi_p = 0.7364$, $E_p = 0.0002$ V) is bigger than the negative value of the net peak current caused by the reductive scan ($\Delta\Phi_p = -0.6849$, $E_p - E^0 = -0.0198$ V).

Fig. 2 demonstrates a qualitative criterion for the estimation of redox state of investigated substance. Note that the ratio C_{Ox}^*/C_{Red}^*

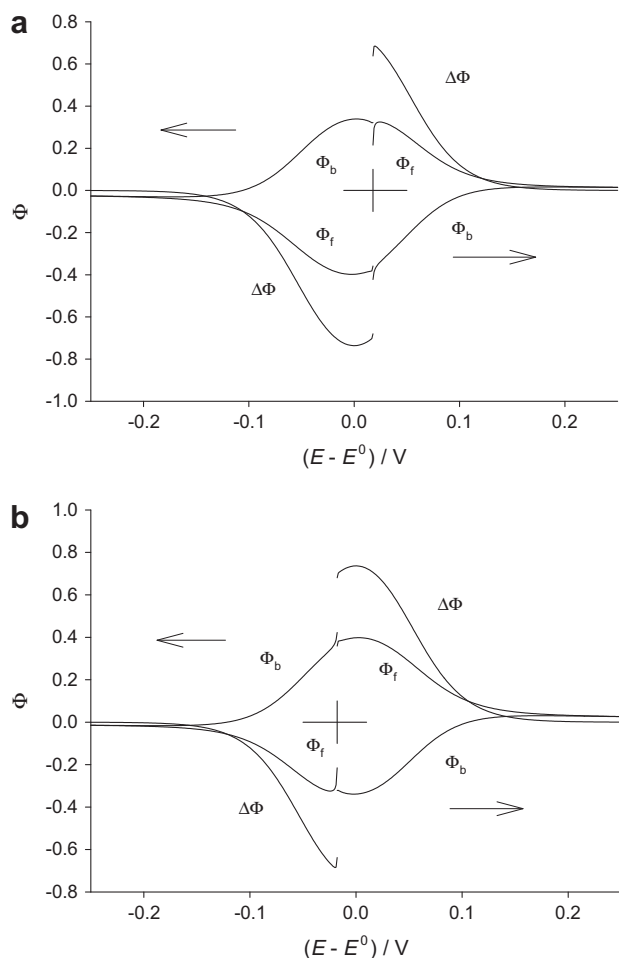can be assessed from the equilibrium potential only if the standard, or formal potential is known. However, the redox state can be calculated from the ratio of peak currents of forward and backward components of better developed response. A linear relationship between $-\Phi_{p,f}/\Phi_{p,b}$ and C_{Ox}^*/C_{Red}^* is shown in Fig. 3. It is calculated from the responses to the oxidative scan under the condition that $C_{Ox}^*/C_{Red}^* < 0.7$ (see Fig. 2B). The relationship satisfies the following equation:

$$-\frac{\Phi_{p,f}}{\Phi_{p,b}} = 1.3187 - 0.2884\frac{C_{Ox}^*}{C_{Red}^*} \tag{13}$$

If $C_{Ox}^*/C_{Red}^* > 1.4$, the ratio $-\Phi_{p,f}/\Phi_{p,b}$ must be measured from the response to the reductive scan (see Fig. 2A). This ratio is a linear function of the ratio C_{Red}^*/C_{Ox}^*:

$$-\frac{\Phi_{p,f}}{\Phi_{p,b}} = 1.3187 - 0.2884\frac{C_{Red}^*}{C_{Ox}^*} \tag{14}$$

In the range $0.7 < C_{Ox}^*/C_{Red}^* < 1.4$ the absolute values of backward components are the biggest at the starting potential (see Fig. 1A). This is also an indication of the redox state of the system.

The experimental application of the above results can be performed, if a value of the equilibrium potential is known. Experimentally, a precise value of the equilibrium potential, of both redox components presented in solution, could be obtained by setting the instrument (potentiostat) in OCP (open circle potential) mode in condition of cyclic voltammetry. Thus, the initial potential is set as the E_{eq}. In other words, regardless of the voltammetric techniques, all voltammograms can then be recorded starting from this potential (in both scan directions). Furthermore, when the E_{eq} is known, the redox state of the system (i.e. C_{Ox}^*/C_{Red}^*) can be estimated from the peak currents ratio (so knowledge of the E^0 is not necessary). This holds for reversible electrode reaction (1). On the other hand, reversibility of the electrode process can be assessed from the current at the starting potential (see Figs. 1, 4 and 5).

Fig. 4 shows SWV responses of quasireversible electrode reaction, calculated for $C_{Ox}^* = C_{Red}^*$, $\kappa = 0.05$ and $\alpha = 0.4$. Electrode kinetics diminishes the forward component and changes the form of the backward component, similarly as the square-wave amplitude does (see Fig. 1B). Also, the kinetics increases the difference between peak potentials of forward components in the reduction and oxidation ($E_{p,f} = -0.066$ V and $E_{p,f} = 0.051$ V, respectively). Furthermore, there is no symmetry in this figure because the transfer
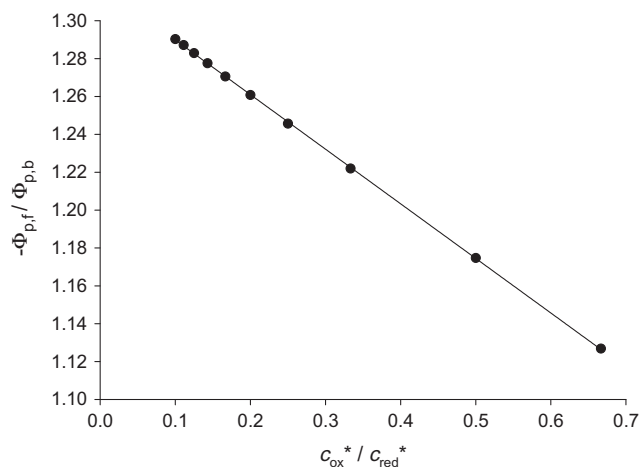

Fig. 2. SWV of reversible electrode reaction. $E_{st} = E_{eq}$, $E_{SW} = 0.050$ V, $dE = \pm0.001$ V, $n = 1$ and $C_{Ox}^*/C_{Red}^* = 2$ (a) and 0.5 (b).

Fig. 3. Dependence of the ratio of peak currents of the forward and backward components of the SWV response to the oxidative scan on the ratio of bulk concentrations of the reactant and product of reversible electrode reaction. $E_{st} = E_{eq}$, $E_{SW} = 0.050$ V, $n = 1$ and $dE = 0.001$ V.
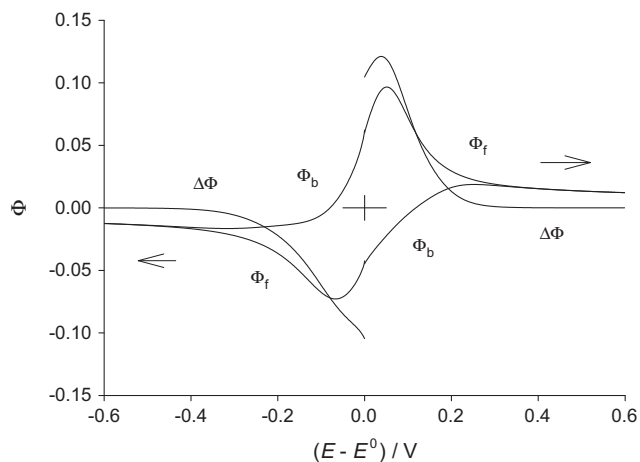
Fig. 4. SWV of kinetically controlled electrode reaction. $E_{st} = E_{eq}$, $C^*_{Ox} = C^*_{Red}$, $n = 1$, $\kappa = 0.05$, $\alpha = 0.4$, $E_{SW} = 0.050$ V and $dE = \pm0.001$ V.
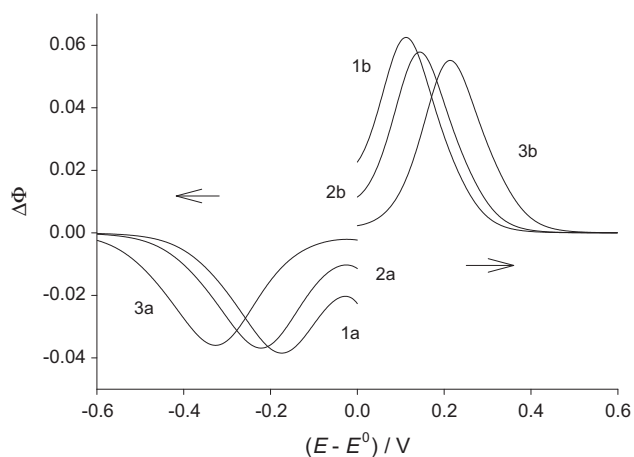

Fig. 5. SWV of irreversible electrode reactions using negative (a) and positive (b) scan directions; $\kappa = 0.01$ (1), 0.005 (2) and 0.001 (3). All other parameters are as in Fig. 4.
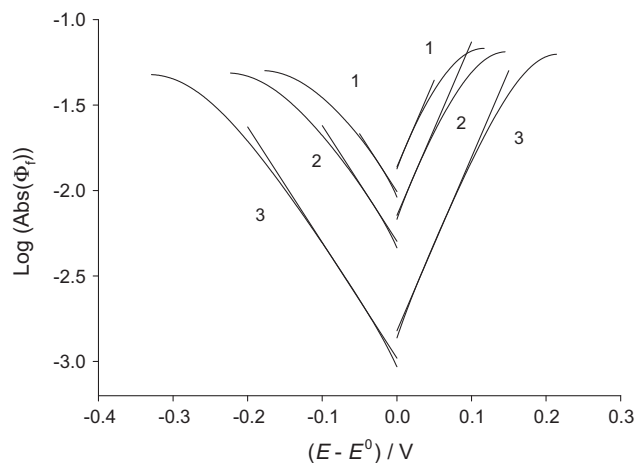

Fig. 6. Tafel plots of forward components of voltammograms shown in Fig. 5.

coefficients of reduction and oxidation are not equal. Finally, it is interesting to note that for $\alpha = 0.4$ the minimum of the net current corresponding to the negative scan direction appears at the starting potential.

The current at the starting potential decreases with the decreasing of the dimensionless kinetic parameter $k = k_s(Df)^{-1/2}$. This is shown in Fig. 5. For irreversible reactions the net peak potentials tend to the linear relationships with the logarithm of the kinetic parameter: $\frac{\Delta E_p}{\Delta \log \kappa} = 2.303RT/\alpha nF$ (for the reductive scan) and $\frac{\Delta E_p}{\Delta \log \kappa} = -2.303RT/(1-\alpha)nF$ (for the oxidative scan). The alternative method for the determination of charge transfer coefficients is to construct Tafel plots using the forward components of the responses to the negative and positive scan directions. An example can be found in Fig. 6. The straight lines in this figure have the following slopes:

$$\frac{\Delta \log(-\Phi_f)}{\Delta E} = -0.4343\frac{\alpha nF}{RT} \tag{15}$$

$$\frac{\Delta \log(\Phi_f)}{\Delta E} = 0.4343\frac{(1-\alpha)nF}{RT} \tag{16}$$

The method applies for $\kappa < 0.005$. The standard rate constant can be estimated from the dependence of the net peak potentials on the logarithm of frequency, as it was demonstrated previously [21].

4. Conclusions

These analyses show that the equilibrium potential can be used as a starting potential in square-wave voltammetry. The advantage of this procedure is the possibility to determine the ratio of bulk concentrations of reactant and product of reversible electrode reaction. Furthermore, the reversibility of electrode reaction can be estimated from the current at the starting potential and the transfer coefficient can be calculated from the relationship between the logarithm of forward component of the response of totally irreversible reaction and the electrode potential.

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