

MATHCAD – A TOOL FOR NUMERICAL CALCULATION OF SQUARE-WAVE VOLTAMMOGRAMS

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An alternative approach for numerical calculation of the square-wave voltammograms using the mathematical programming package MATHCAD is presented. A quasi-reversible redox reaction is considered and a mathematical model is developed under conditions of the square-wave voltammetry (SWV). Application of the mathematical model in MATHCAD is discussed and the file used for numerical simulation is presented. The relationships between the properties of the SW response and the parameters of both the quasireversible redox reaction and the excitation signal are discussed.

Key words: MATHCAD; square-wave voltammograms; numerical calculation

INTRODUCTION

Numerical simulation of the voltammetric response of particular voltammetric technique is a common approach in the development of the voltammetric method's theory. Studying the numerically simulated data one can predict the behavior of the voltammetric experiment. Moreover, comparing and fitting the experimental and theoretical data, important kinetic parameters of the investigated redox system, such as the standard rate constant k_s and the coefficient of electron transfer α , can be estimated. For all these reasons, a large number of scientific papers are dedicated to this important subject [1].

Additionally, numerous specialized programming packages for simulation of the voltammetric response of various techniques are already available on the market. It is, however, still of interest to develop simple and flexible methods for calculation of the theoretical response of various voltammetric techniques. Nowadays, most chemists are familiar with the general purpose multitasking programming packages such as EXCEL, QPRO, LOTUS, MATHCAD, etc. Therefore, it is very useful to find a way for calculation of the voltammetric responses using these programming packages.

In this paper an alternative approach for calculation of the square-wave voltammetric response of

a quasi-reversible redox reaction, using the programming package MATHCAD, is presented. MATHCAD is one of the best general purpose mathematical programming packages [2]. The program is user-friendly, fast and precise. It should be emphasized that the program provides various numerical methods which are necessary for development of voltammetric method's theory.

As was mentioned previously, the voltammetric curves are numerically simulated under conditions of the square-wave voltammetry, which is one of the most advanced electroanalytical techniques [3]. The square-wave voltammetry is a complex, multi-step chronoamperometric method. The excitation signal used in SW voltammetry is a train of cathodic and anodic pulses superposed on a staircase potential ramp (see Fig. 1a). One potential cycle in the SWV is presented in the Fig. 1b. The parameters of the signal are: the square-wave frequency f , which is the inverse value of the duration of the potential cycle $f = 1/\tau$ (see Fig. 1b), the SW amplitude E_{sw} , which is the half of the peak-to-peak height, and the scan increment dE , which is the step of the staircase ramp.

The current is measured at the end of each potential pulse. All the currents measured at the end

of the cathodic pulses create the forward (cathodic) component Ψ_f , while the currents measured at the end of the anodic pulses, create the backward (anodic) component Ψ_b of the SW response (see Fig.

1c). The net-response Ψ_{net} is calculated as a difference between the two successive cathodic and anodic currents: $\Psi_{net} = \Psi_f - \Psi_b$.

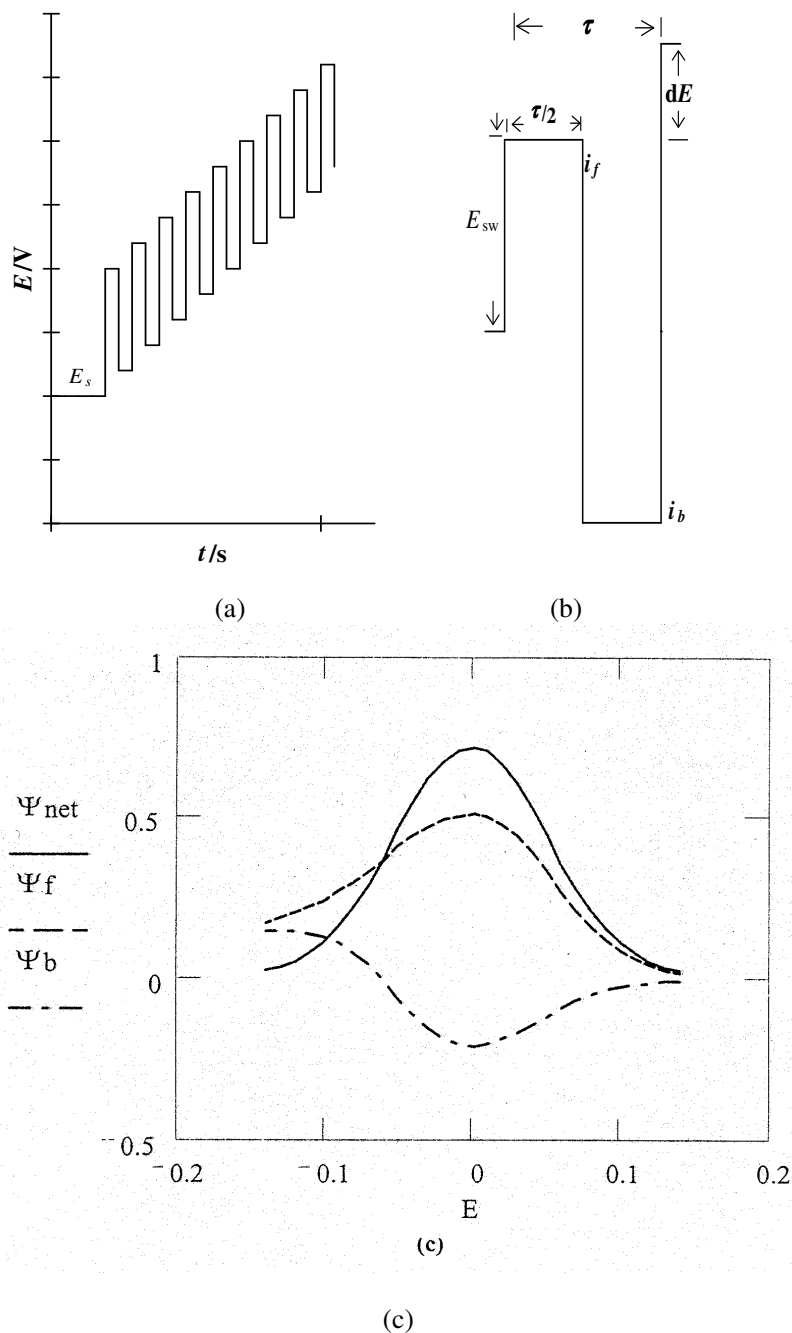
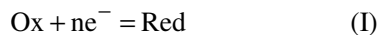


Fig. 1. (a) The scheme of the excitation signal used in the square-wave voltammetry. (b) One potential cycle in the square-wave voltammetry. (c) A typical square-wave dimensionless voltammetric response for a reversible redox reaction.

E_s – the starting potential; E_{sw} – the SW amplitude; dE – the scan increment; τ – the duration of one potential cycle; i_f and i_b – the forward and the reverse real currents; Ψ_f , Ψ_b , Ψ_{net} – the forward, the backward and the net dimensionless components of the SW response.

MATHEMATICAL MODEL

A quasireversible redox reaction of two chemically stable species is considered:



It is assumed that the mass transport occurs through planar, stationary, and semi-infinite diffusion model. The redox reaction (I) is described mathematically with the following set of differential equations:

$$\delta c_{\text{Ox}} / \delta t = D(\delta^2 c_{\text{Ox}} / \delta x^2) \quad (1)$$

$$\delta c_{\text{Red}} / \delta t = D(\delta^2 c_{\text{Red}} / \delta x^2) \quad (2)$$

For the meaning of the symbols and abbreviations see the Table I. For simplicity, the diffusion coefficients of both species Ox and Red are supposed to be equal.

At the very beginning of the experiment, only the Ox form of the redox couple is present in the electrolyte solution. Hence, the above differential equations are solved with the following initial and boundary conditions:

$$t = 0: \quad c_{\text{Ox}} = c_{\text{Ox}}^*; \quad c_{\text{Red}} = 0 \quad (\text{a})$$

$$t > 0, x \rightarrow \infty: \quad c_{\text{Ox}} \rightarrow c_{\text{Ox}}^*; \quad c_{\text{Red}} \rightarrow 0 \quad (\text{b})$$

$$t > 0, x = 0: \quad D(\delta c_{\text{Ox}} / \delta x)_{x=0} = -D(\delta c_{\text{Red}} / \delta x)_{x=0} = i / (nFS) \quad (\text{c})$$

Since the redox reaction is partly controlled by the charge transfer rate, at the electrode surface, the following condition is valid:

$$i / (nFS) = k_s \exp(-\alpha\phi) [(c_{\text{Ox}})_{x=0} - (c_{\text{Red}})_{x=0} \exp(\phi)] \quad (3)$$

where ϕ is dimensionless relative electrode potential: $\phi = (nF)(E - E^0_{\text{Ox/Red}}) / (RT)$. The solutions which relate the concentrations of both species Ox and Red at the electrode surface with the current, were obtained applying Laplace transforms:

Table I

List of symbols and abbreviations

Ox	– oxidized form of electroactive species
Red	– reduced form of electroactive species
c_{Ox}	– concentration of Ox species anywhere in the solution
c_{Red}	– concentration of Red species anywhere in the solution
c_{Ox}^*	– concentration of Ox species in the bulk of the solution
$(c_{\text{Ox}})_{x=0}$	– concentration of Ox species at the electrode surface
$(c_{\text{Red}})_{x=0}$	– concentration of Red species at the electrode surface
t	– time
x	– distance from the electrode
i	– current
n	– number of electrons
F	– Faraday constant
S	– electrode surface area
k_s	– standard kinetic rate constant of the redox reaction
α	– coefficient of electron transfer
T	– thermodynamic temperature
R	– universal gas constant
E	– electrode potential
E^0	– standard redox potential of the Ox/Red couple
D	– diffusion coefficient
Ψ_1	– dimensionless current at the very first time increment
Ψ_j	– dimensionless current at the j-th time increment
Ψ_f	– dimensionless forward current
Ψ_b	– dimensionless backward current
Ψ_{net}	– dimensionless net current
K	– dimensionless kinetic parameter
f	– SW frequency
E_{sw}	– SW amplitude
dE	– scan increment
ΔE	– potential interval
E_s	– starting potential vs. E^0

$$(c_{\text{Ox}})_{x=0} = c_{\text{Ox}}^* - \frac{1}{\sqrt{\pi}} \cdot \int_0^t \frac{i}{n \cdot F \cdot S \cdot \sqrt{D}} \cdot (t - \tau)^{\frac{1}{2}} d\tau \quad (4)$$

$$(c_{Red})_{x=0} = \frac{1}{\sqrt{\pi}} \cdot \int_0^t \frac{i}{n \cdot F \cdot S \cdot \sqrt{D}} \cdot (t - \tau)^{-\frac{1}{2}} d\tau \quad (5)$$

A combination of the eqs. (3) – (5) gives the following integral equation:

$$\frac{i}{n \cdot F \cdot S} = k_s \cdot e^{-\alpha \phi} \cdot \left[c_{Ox}^* - \int_0^t \frac{i}{n \cdot F \cdot S \cdot \sqrt{D \cdot \pi}} \cdot (t - \tau)^{-\frac{1}{2}} d\tau - e^{\phi} \cdot \int_0^t \frac{i}{n \cdot F \cdot S \cdot \sqrt{D \cdot \pi}} \cdot (t - \tau)^{-\frac{1}{2}} d\tau \right] \quad (6)$$

The above integral equation relates the current with time at a certain potential. The solution of the last integral equation under conditions of the SW voltammetry was obtained by the numerical method of Nicholson and Olmstead [1]. Both the time variable t

and dimensionless current $\Psi = i(nFSc_{Ox}^*)^{-1}(fD)^{-1/2}$ are discretized. To each $t = jd$, where d is the time increment, a certain Ψ_j can be ascribed. The numerical solution is represented with the following recursive formulae:

$$\Psi_1 = \frac{K \cdot e^{-\alpha \phi_1}}{1 + 2 \cdot K \cdot \left[(50 \cdot \pi)^{\frac{1}{2}} \cdot (1 + e^{\phi_1}) \right] \cdot e^{-\alpha \phi_1}} \quad (7)$$

$$\Psi_j = \frac{K \cdot e^{-\alpha \phi_j} \cdot \left[1 - 2 \cdot (50 \cdot \pi)^{\frac{1}{2}} \cdot (1 + e^{\phi_j}) \cdot \sum_{i=1}^{j-1} \Psi_i \cdot S_{j-i+1} \right]}{1 + 2 \cdot K \cdot \left[(50 \cdot \pi)^{\frac{1}{2}} \cdot (1 + e^{\phi_j}) \right] \cdot e^{-\alpha \phi_j}} \quad (8)$$

where $S_1 = 1$, $S_k = (k)^{1/2} - (k-1)^{1/2}$ while $K = k_s / (fD)^{1/2}$ is dimensionless kinetic parameter. For this calculation, the time increment $d = (50f)^{-1}$ was

used, which means that each SW half-period $\pi/2$ (see Fig. 1b) was divided in 25 increments.

SOLVING THE MATHEMATICAL MODEL USING THE PROGRAMMING PACKAGE “MATHCAD”

The MATHCAD file used for calculation of the dimensionless SW voltammograms is given in the Fig 2. At the very beginning of the file, all the constant parameters which are needed for numerical calculations, are defined.

For numerical integration, the entire time of the SW excitation signal is divided in the finite number of time increments. In the previous chapter, it was mentioned that the time increment d is related to the SW frequency through the formula $d =$

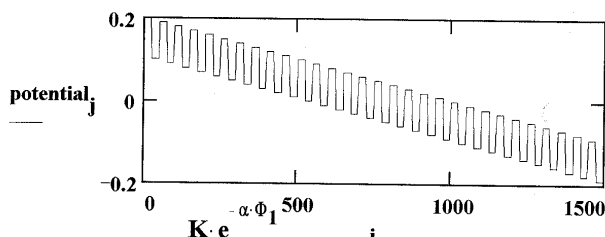
$(50f)^{-1}$. It means that each potential cycle in the SW voltammetry is divided in 50 increments. The number of the potential cycles depends on the potential interval ΔE and the scan increment dE . The total number of the potential cycles is equal to the ratio $\Delta E/dE$. Therefore, the total number of the time increments is $(\Delta E/dE) \cdot 50$, while the ordinary number of each time increment is ranged within the interval of 1 to $(\Delta E/dE) \cdot 50$ (see equation (I) in Fig. 2).

$E_s := 0.15 \Delta E := 0.3 \quad dE := 0.01 \quad E_{sw} := 0.05 \quad K := 10$

$n := 1 \quad F := 96500 \quad R := 8.314 \quad T := 298.15 \quad \alpha := 0.5$

$j := 1.. \frac{\Delta E}{dE} \cdot 50 \quad (I)$

$potential_j := E_s + E_{sw} - \left[\left(\text{ceil} \left(\frac{j-1}{25} \right) \cdot dE + \text{if} \left(\frac{\text{ceil} \left(\frac{j}{25} \right)}{2} = \text{ceil} \left(\frac{j-1}{25} \right), 1, -1 \right) \cdot E_{sw} + E_{sw} \right) - dE \right] \quad (II)$



Plot 1

$\Phi_j := n \cdot \frac{F}{R \cdot T} \cdot potential_j \quad (III)$

$k := 2.. \frac{\Delta E}{dE} \cdot 50$

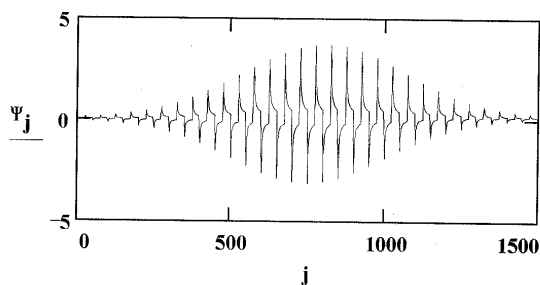
$S_k := \sqrt{k} - \sqrt{k-1}$

$\Psi_1 := \frac{j}{1 + 2 \cdot K \cdot \left[\frac{1}{(50 \cdot \pi)^2} \cdot \left(1 + e^{\Phi_1} \right) \right] \cdot e^{-\alpha \Phi_1}}$

(IV)

$\Psi_k := \frac{K \cdot e^{-\alpha \Phi_k} \cdot \left[1 - 2 \cdot (50 \cdot \pi)^2 \cdot \left(1 + e^{\Phi_k} \right) \cdot \sum_{i=1}^{k-1} \Psi_i \cdot S_{k-i+1} \right]}{1 + 2 \cdot K \cdot \left[\frac{1}{(50 \cdot \pi)^2} \cdot \left(1 + e^{\Phi_k} \right) \right] \cdot e^{-\alpha \Phi_k}}$

(V)



Plot 2

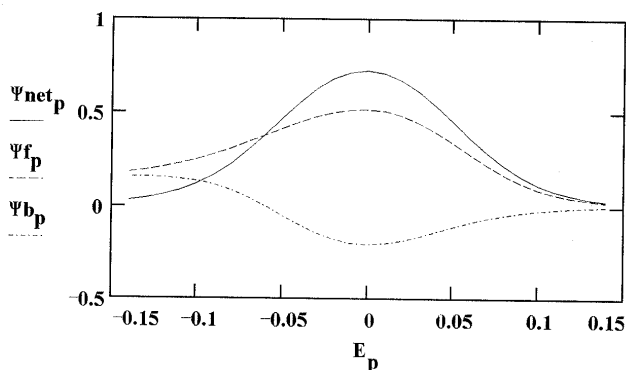
$p := 1.. \left(\frac{\Delta E}{dE} \right) - 1$

$\Psi_{b_p} := \Psi_{50 \cdot p + 25} \quad VI$

$\Psi_{f_p} := \Psi_{(p+1) \cdot 50} \quad VII$

$\Psi_{net_p} := \Psi_{f_p} - \Psi_{b_p} \quad VIII$

$E_p := E_s - p \cdot dE \quad IX$



Plot 3.

Fig. 2. The MATHCAD file created for numerical simulation of the SW voltammograms of a quasi-reversible redox reaction

Creating the file, a crucial step is development of a function which simulates the potential waveform used in the SW voltammetry. MATHCAD has a database of various mathematical functions, however, neither of them resembles the shape of the SW excitation signal. Nevertheless, the problem can be solved if the mathematical "step" function is appropriately combined with the logical "if" function. The new function, called "potential", is defined by the eq. (II) in the Fig. 2 and is of exactly the same form as the SW excitation signal (see the Plot 1 in the Fig. 2). This function represents the relative electrode potential applied to the working electrode under conditions of the SW voltammetry. Using this function, one can readily defines the dimensionless potential used for numerical calculations $\phi = nF(E - E^0)/(RT)$.

The calculation of the dimensionless response under conditions of the SW voltammetric experiment was carried out by the recursive formulae (IV) and (V) in the Fig. 2. The eq. (V) calculates the dimensionless current Ψ_k at each potential pulse applied to the working electrode. Above these formulae, the S_k factor needed for numerical integration is defined. After processing of the formulae (IV) and (V), a new plot is created (see Plot 2 in the Fig.1) which shows the variation of the current with time at each SW potential pulse.

As it was mentioned previously, according to the current-sampling procedure used in the SW volt-

ammetry, only the current obtained at the end of a single potential pulse is measured. The reason is to discriminate the capacitive current during the measurement and to increase the sensitivity of the technique [3]. Hence, all the currents measured at the end of all the cathodic pulses create the forward branch Ψ_f of the SW voltammogram. The backward branch Ψ_b contains the currents measured at the end of each anodic pulse. The net current Ψ_{net} is defined as a difference between the forward and backward current. Therefore, one needs to select only the currents obtained at the end of the each SW pulse. This can be done with the set of formulae from (VI) to (VIII) given in the Fig. 2.

Finally it should be noted, that in the SW voltammetry, the current data are plotted versus the potential values of the staircase ramp. The last formulae of the file (IX) defines the potential of the staircase ramp. Plot 3 in the Fig. 2 represents the numerically calculated SW voltammetric response of the quasireversible redox reaction.

The processing time for calculation of a single SW voltammogram depends on the performance of the used processor, potential interval and the scan increment. With the processor PC 486DX2/66 MHz with 8 MB RAM memory, potential interval $\Delta E = 0.3$ V and scan increment is $dE = 5$ mV, processing time takes about 5 min. The processing time can be markedly decreased with increase of the scan increment.

DISCUSSION OF THE NUMERICALLY CALCULATED DATA

The MATHCAD file was utilized for numerical simulation of about hundred SW voltammograms, in order to investigate the relationships between the properties of the response and the parameters of both the redox reaction and the excitation signal.

As can be seen from the Plot 3 in the Fig. 2, the SW voltammograms are current-potential bell-shaped curves characterized with the dimensionless peak current $\Delta\Psi_p$, the peak potential E_p and the half-width of the peak $\Delta E_{p/2}$. The number of points constituting a single voltammogram depends on the scan increment dE . The point with the highest current value determinates the peak current $\Delta\Psi_p$, while its position at the potential axis defines the peak potential E_p . The width of the peak at its half height, expressed in Volts, is called the half-width of the peak $\Delta E_{p/2}$.

According to the eq. (8), the dimensionless SW response of the quasi-reversible redox reaction (I) is mainly dependent on the kinetic parameter K and the electron transfer coefficient α . The apparent reversibility of the redox reaction entirely depends on the kinetic parameter $K = k_s / (Df)^{1/2}$. The influence of this parameter to the dimensionless peak current is presented in the Fig. 3. If the redox reaction appears either irreversible ($\log K \leq -1.5$), or reversible ($\log K \geq 0.75$), the dimensionless peak current does not depend on the kinetic parameter (see Fig. 3). Within the region $-1 \leq \log K \leq 0.3$ the redox reaction appears quasi-reversible, and the dimensionless peak current depends linearly on the kinetic parameter K . The slope of this linear portion is determined by the particular value of the transfer coefficient α (see Fig. 3).

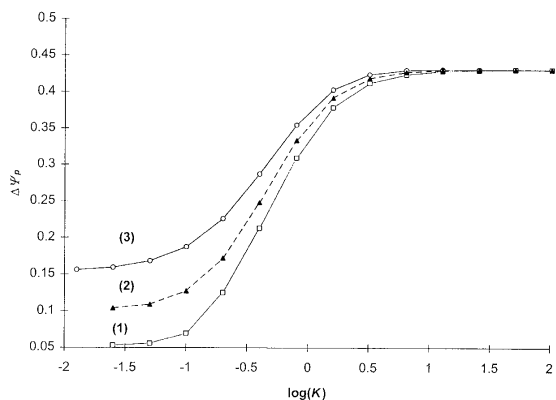


Fig. 3. The effect of the kinetic parameter K on the dimensionless SW peak currents for divers values of the transfer coefficient α . The conditions of the simulation were: $E_{sw} = 0,025$ V; $dE = 0,005$ V; $T = 298,15$ K; $\alpha = 0.3$ (1); 0.5 (2) and 0.7 (3)

The position of the SW peak is also sensitive to the kinetic parameter K . The relationship between the peak potentials E_p and the logarithm of the kinetic parameter K , for different values of the transfer coefficient α , is presented in the Fig. 4. If the redox reaction is close to the reversible region ($\log K \geq 0.5$), the peak potential becomes almost independent on the kinetic parameter. Only within the irreversible region, the peak potential depends linearly on the logarithm of K . The slope of the linear portion is dependent on the transfer coefficient α and it is defined by the following equation: $\Delta E_p / \Delta \log K = 2,303 RT / (\alpha n F)$. Therefore, if the irreversibility of the redox reaction was reached experimentally, this equation could be utilized for an estimation of the transfer coefficient.

The half-width of the SW peak gradually changes with the alteration of the kinetic parameter K . If the redox reaction appears irreversible, the half-width of its SW peak is solely determined by the transfer coefficient α , through the equation: $\Delta E_{p/2} = (90 \pm 2) / (\alpha n)$ mV. Within the quasi-reversible region, the half-width of the peak decreases proportionally with increase of the kinetic parameter K , reaching a constant value for the reversible redox reaction. If the SW amplitude was $E_{sw} = 50$ mV, the half-width of the peak for reversible redox reaction is $\Delta E_{p/2} = 125$ mV.

Numerical simulations shown that the SW peak current depends linearly on the SW amplitude (see Fig. 5). The peak potential remained virtually unchanged with the variation of the amplitude from 2 to 100 mV. The half-width of the peak enhances

slightly with the increase of the SW amplitude. It is important to note that the ratio $\Delta \Psi_p / \Delta E_{p/2}$ reaches the maximum value for $E_{sw} = 90$ mV, which means that this amplitude is the most suitable for analytical purposes.

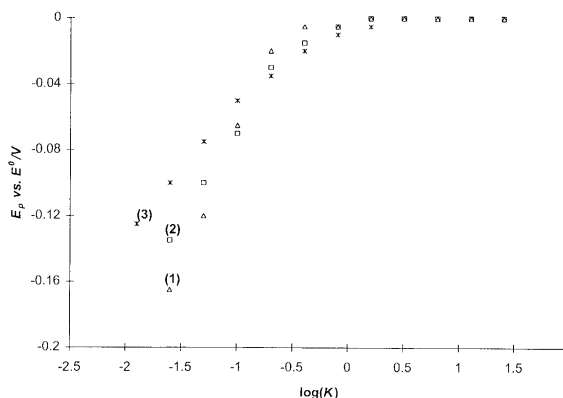


Fig. 4. The effect of the kinetic parameter K on the SW peak potentials for divers values of the transfer coefficient α . The conditions of the simulation were: $E_{sw} = 0,025$ V; $dE = 0,005$ V; $T = 298,15$ K; $\alpha = 0.4$ (1); 0.5 (2) and 0.7 (3)

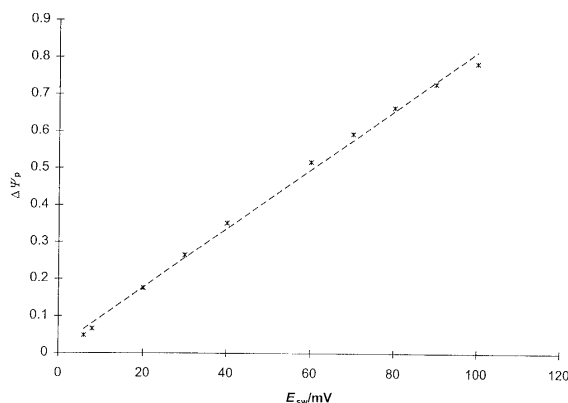


Fig. 5. The dependence of the peak currents on the SW amplitude. The conditions of the simulations were: $\log K = -0,5$; $\alpha = 0,5$; $dE = 5$ mV; $T = 298,15$ K

When particular redox reaction is investigated experimentally, the variation of the kinetic parameter K , which is defined as $K = k_s / (Df)^{1/2}$, can be attained by an alteration of the frequency f of the excitation signal. Therefore, the effect of the SW frequency on the SW response can be understood through the previously discussed effect of the kinetic parameter K .

CONCLUSION

In this paper it is demonstrated that the MATHCAD programming package can be successfully used as a tool for numerical calculation of the square-wave voltammograms. It is shown that this program can easily generate a complex function which possesses exactly the same shape as the SW excitation signal. The presented MATHCAD file

reflects the simplicity in which one can communicate with the program.

Studying the numerically simulated voltammograms one can understand the behavior of the voltammetric experiment and realize the relationships between the properties of the investigated redox reaction and the features of the voltammetric response.

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Резиме

НУМЕРИЧКО СИМУЛИРАЊЕ НА КВАДРАТНО-БРАНОВИ ВОЛТАМОГРАМИ СО МАТНСАД

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Клучни зборови: МATHCAD; квадратно-бранови волтамограми; нумерички пресметки

Презентиран е алтернативен начин за нумеричко симулирање на квадратно-бранови волтамограми со примена на математичкиот програмски пакет МATHCAD. Развиен е математички модел за квазиреверзибилна редокс-реакција во услови на квадратно-бранова волтаметрија. Дискутиран е начинот на кој може математичкиот модел да биде инкорпориран во програмскиот пакет МATHCAD. Покрај тоа, прика-

жана е комплетната датотека што е користена за симулирање на ексцитациониот сигнал и за нумеричко симулирање на волтаметрискиот одговор. Проучени се теоретските функционални зависимости помеѓу параметрите на квадратно-брановиот одзив и кинетичките параметри на редокс-реакцијата, како и параметрите на ексцитациониот сигнал.