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# Cyclic multipulse voltammetric techniques. Part II: EC mechanism

# Dijana Jadreško\*, Marina Zelić

Division for Marine and Environmental Research, Ruđer Bošković Institute, P.O. Box 180, HR-10002 Zagreb, Croatia

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### ABSTRACT

A theoretical analysis of electrode processes controlled by kinetics of follow-up homogeneous chemical reaction under conditions of (simple) cyclic multi pulse voltammetry (CMPV), cyclic differential multi pulse voltammetry (CDMPV) and cyclic square-wave voltammetry (CSWV) is presented. The study was performed under linear diffusion conditions and for equal diffusion coefficients of all participants of the electrode process. Chemical reaction changes the shape and position of CMPV response, compared to a simple reversible electrode reaction. As the chemical process becomes faster, forward/reduction wave decreases whereas a pronounced maximum appears on it. On the other hand, the influence of following chemical reaction on the shape of CDMPV and CSWV reduction signal is not significant, while their voltammograms shifted towards more positive potentials as well. Experimentally, the rate constant of follow-up chemical reaction ( $k_f$ ) can be estimated from the linear dependence of limiting to maximum reduction currents ratio ( $i_{1,c}/i_{max,c}$ ) on  $\log(t_p)$  in CMPV, as well as of anodic to cathodic net peak currents ratio ( $\Delta i_{p,a}/\Delta i_{p,c}$ ) on  $\log(t_p)$  in CDMPV and  $\log(f)$  in CSWV. Combination of two or more cyclic multipulse voltammetric techniques gives more information about kinetics i.e. more precise determination/ estimation of the rate constant of follow-up chemical reaction of follow-up chemical reaction, compared with application of only one technique.

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## 1. Introduction

Since pulse voltammetric techniques were first introduced [1] (especially during the last several decades), the study of homogeneous chemical reactions coupled to electrode processes was and still is one of the main subjects in electrochemistry [2–4]. In the late seventies Ryan [5] developed a theory of cyclic staircase voltammetry (CSV) for the study of kinetics and mechanisms of electrode processes. He showed [5] that disappearance of reduction product, in case of an EC mechanism, could be recognized from decreased peak current on the reverse branch of cyclic staircase voltammogram. More exactly, the ratio between anodic and cathodic peak currents (i.e. between their absolute values) is lower than unity for an EC mechanism and equal to unity for a reversible E mechanism. Furthermore, when the mechanism is known, the rate constant of chemical reaction following the charge transfer can be determined either from the ratio of anodic to cathodic peak currents [5-7] or from the peak potential shift (if  $E^0$  is known and the chemical reaction is so fast that no anodic signal is seen). However cyclic voltammetry has several limitations, comparing with pulse voltammetric techniques, due to its low sensitivity and low resolution of signals. On the other hand, modern pulse voltammetric techniques include scanning in only one direction (negative or positive) which means that only reduction (or oxidation) process can be studied.

Laborda et al. [4,8,9] gave several diagnostic tests for recognition of the reaction mechanism from characteristic parameters of the voltammograms obtained by different pulse techniques. *CE* and *EC* mechanisms can be distinguished from other processes (e.g. reversible *E* mechanism, catalytic mechanism) by following the changes of the peak (or half-wave) potential due to variations of the electrode radius, chemical kinetics or pulse duration. According to Osteryoung and coworkers [10], for a chemical reaction that follows reversible charge transfer, SWV reduction peak potential shifts to more positive values, whereas the peak current decreases to a constant value as the reaction becomes faster, due to the increased consumption of the reduction product by the chemical reaction.

In a previous article [11], we demonstrated that cyclic scan could generally be combined with a pulse technique so to give cyclic (multi) pulse voltammetry. Theoretical and experimental studies of (simple) electrode kinetics were performed using cyclic pulse voltammetry, cyclic differential pulse voltammetry and cyclic square-wave voltammetry. It is important to stress that for all such measurements a commercially available instrument and its original software were applied.

Concerning the names of the new cyclic techniques, two approaches are possible. The first of them takes into account their origin and "traditional" names of the corresponding "simple"







<sup>\*</sup> Corresponding author. Tel.: +385 14561181. *E-mail address: djadresko@irb.hr* (D. Jadreško).

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techniques. In such a way, before mentioned cyclic pulse voltammetry, cyclic differential pulse voltammetry and cyclic square wave voltammetry were named. In some recent papers [12,13] however, modified names of some simple (i.e. non-cyclic) techniques were proposed. Under reviewer's influence we introduced such type of names (i.e. cyclic multi pulse voltammetry and cyclic differential multi pulse voltammetry) during corrections of our previous article [11]. To an average electrochemist, who did not read Ref. [12], or some other articles from the same group, this sounds strange. However, it is enough to accept that differential multi pulse voltammetry, for example, is a synonym for "modern" version of DPV (i.e. technique characterized by continuous stepwise excitation signal to which potential pulses of constant amplitude are superimposed) [14] and the name of the corresponding cyclic technique, becomes clear.

In this communication, the application of cyclic multi pulse voltammetry (CMPV), cyclic differential multi pulse voltammetry (CDMPV) and cyclic square-wave voltammetry (CSWV) in the study of kinetics of a (pseudo)first order homogeneous chemical reaction, that involves the product of charge transfer process, is given. The theoretical investigations of the influences of timing/ kinetic parameters on the cyclic multipulse voltammograms for *EC* reaction mechanisms, under conditions of linear diffusion and with equal diffusivities for all the species included in process, were also studied.

From such analyses, there arise simple diagnostic criteria for elucidation of the mechanism of electrode reactions taking place at planar electrode, as well as the estimation of the rate constant of a follow-up chemical reaction.

#### 2. A model

The applied cyclic (multi)pulse voltammetric techniques are based on the potential-time waveforms defined in Fig. 1.

A simple, reversible electron transfer followed by irreversible homogenous chemical reaction on the stationary, planar electrode is considered:

$$Ox_{(aq)} + ne^{-} \rightleftharpoons Red_{(aq)} \xrightarrow{\kappa_{f}} P_{(aq)}$$
<sup>(1)</sup>

where  $k_f(s^{-1})$  denotes the rate constant of chemical reaction and *P* is the electroinactive product. Most frequently,  $k_f$  is a pseudo-firstorder rate constant defined as  $k_f = k_{f,r} * c_X^*$ , where  $k_{f,r}$  is the real second-order rate constant in units of mol<sup>-1</sup> dm<sup>3</sup> s<sup>-1</sup> and  $c_X^*$  is the concentration of a reactant X (e.g. solvent) present in great excess over Ox species.

It is assumed that all participants of the electrode process are soluble in aqueous electrolyte solution and cannot be adsorbed on the electrode surface. Initially only the reactant Ox is present in the solution. For semi-infinite diffusion the following system of differential equations and boundary conditions has to be solved:

$$\frac{\partial c_{\text{Ox}}}{\partial t} = D \frac{\partial^2 c_{\text{Ox}}}{\partial x^2}; \quad \frac{\partial c_{\text{Red}}}{\partial t} = D \frac{\partial^2 c_{\text{Red}}}{\partial x^2} - k_f \cdot c_{\text{Red}}$$
(2)

$$t = 0, \ x \ge 0: \quad c_{0x} = c_{0x}^*, \ c_{Red} = c_P = 0$$
 (3)

$$t > 0, \ x \to \infty: \quad c_{Ox} \to c^*_{Ox}, \ c_{Red} \to 0, \ c_P \to 0$$
 (4)

$$x = 0: \quad D\left(\frac{\partial c_{0x}}{\partial x}\right)_{x=0} = -D\left(\frac{\partial c_{\text{Red}}}{\partial x}\right)_{x=0} = -\frac{i}{nFS}$$
(5)

$$D\left(\frac{\partial c_P}{\partial x}\right)_{x=0} = 0 \tag{6}$$

$$(c_{\text{Ox}})_{x=0} = \exp(\varphi) \cdot (c_{\text{Red}})_{x=0}$$
(7)

The application of Feldberg's finite difference approximation [15] to Eq. (5) gives the expression:

$$\frac{\cos(1) - \cos(0)}{\Delta x/2} = -\frac{\operatorname{cred}(1) - \operatorname{cred}(0)}{\Delta x/2} = -\frac{i}{nFSc_{0x}^*D}$$
(8)

where symbols cox(0) and cred(0) denote the dimensionless concentrations of Ox and Red species at the electrode surface, respectively. The symbols cox(1) and cred(1) correspond to dimensionless concentrations of Ox and Red species in the middle of the first space increment.

Introducing Eq. (8) into Eq. (7) yields the expression for the "operating" dimensionless current:

$$\frac{i\Delta t}{nFSc_{Ox}^*\Delta x} = -2\frac{dd}{1+e^{\varphi}}[cox(1) - e^{\varphi}cred(1)]$$
(9)

where  $dd = D\Delta t/\Delta x^2 = 0.4$  is a common dimensionless diffusion coefficient,  $\Delta t$  and  $\Delta x$  are the time and space increments, respectively,  $\varphi = nF(E - E^0)/RT$  is dimensionless potential. The meanings of all symbols are given in Table 1.

The dimensionless CMPV current was calculated by using  $\Delta t = t_p/50$  and multiplying Eq. (9) with  $5\sqrt{2\pi}/\sqrt{dd}$ , while in CDMPV dimensionless current was calculated by using  $\Delta t = t_p/25$  and multiplying Eq. (9) with  $5\sqrt{\pi}/\sqrt{dd}$ :

$$\Phi = i\sqrt{\pi t_p}/(nFSc_{\rm Ox}^*\sqrt{D}) \tag{10}$$

The similar expression for the dimensionless CSWV current was obtained by using  $\Delta t = \tau/25$  where  $\tau \equiv t_p = 1/2f$  (i.e. each square-wave half-period is divided into 25 time increments) and multiplying Eq. (9) with  $5\sqrt{2}/\sqrt{dd}$ :

$$\Phi = i/(nFSc_{Ox}^*\sqrt{Df}) \tag{11}$$

In the case of *EC* mechanism (1), current response generally depends on the dimensionless chemical kinetic parameter  $K_c = k_f t_p$  (or  $K_c = k_f \cdot (2f)^{-1}$ ).

#### 3. Results and discussion

In the recent paper [11] chemical inactivity of the reduction product, Red, was assumed. However, in real conditions, products of many electron transfer processes are very reactive species, ready for further reactions on the electrode surface or in solution. Accordingly, electrochemical processes may involve multiple reaction steps, which can be chemical (*C*) or electrochemical (*E*) in nature [14,16]. The most common electrode processes followed by chemical reactions are: solvent/ligand exchange, metal ion complexation, disproportionation, protonation/deprotonation, etc.

#### 3.1. Cyclic multi pulse voltammetry (CMPV)

Considering the electrode process (1), a theoretical influence of dimensionless chemical kinetic parameter,  $K_c = k_f t_p$ , was investigated for the following set of standard parameters: n = 1,  $t_{\rm d} = 0.4$  s,  $t_{\rm p} = 50$  ms,  $\Delta E = 2$  mV,  $E_{\rm st} = 0.4$  V vs.  $E^0$ ,  $E_{\rm S} = -0.4$  V vs.  $E^0$ . The influence of follow-up chemical reaction on cyclic multipulse voltammograms is manifested by decreasing the absolute values of limiting cathodic and anodic currents (and their ratio, i.e.  $\Phi_{l,a}/\Phi_{l,c}$ ) with disappearance of reverse branch of CMP voltammogram for the values of  $K_c > 10^{-3}$  (i.e.  $k_f > 0.02 \text{ s}^{-1}$  if  $t_p = 50 \text{ ms}$ ) (Fig. 2). Accordingly, the reverse branch of CMPV response gives the information on stability of the redox product, Red, i.e. insight into the mechanism of electrode process. This is in accordance with the literature results [9]. Furthermore, it is evident that by increasing the value of  $K_c$ , i.e. under the influence of follow-up chemical reaction, the shape of forward/cathodic branch of CMP voltammogram changes significantly. Initial sigmoidal response is gradually



**Fig. 1.** Excitation signals in cyclic multi pulse voltammetry (CMPV), cyclic differential multi pulse voltammetry (CDMPV) and cyclic square-wave voltammetry (CSWV). Sampling points are schematically indicated for each technique.  $\Delta E$  = step potential,  $t_d$  = interval time,  $t_p$  = pulse time,  $E_{DMPV/SW}$  = pulse amplitude,  $\tau$  = time between pulses ( $\tau = t_d - t_p$ ).

transformed to the signal that could be described as a wave with more or less pronounced maximum and poorly defined limiting current or even as an asymmetric peak. In other words, characteristics of an *EC* mechanism (in CMP voltammetry) are occurrence of the current maximum and decrease of the limiting reduction current. Both these values are lower than the limiting current of the wave that reflects a simple reversible electrode reaction.

In Fig. 2A, eleven different cyclic multipulse voltammograms are given, but some of them are not clearly visible. It is because, for low values of  $K_{c_1}$  cathodic branches are nearly identical whereas anodic waves differ significantly. On the other hand, high values of the chemical kinetic parameter "produces" the CMP voltammograms without pronounced reoxidation waves, i.e. with virtually identical reverse branches. For  $K_c \ge 0.1$ , the cathodic branch of CMPV response apparently looks like the forward branch of a cyclic staircase voltammogram (see inset in Fig. 2A). The maximum on forward branch of CMP voltammogram is caused by diminishing of the product reoxidation between two pulses (at  $E = E_{st}$ ), because a part of Red is transformed to P. The shift of cathodic wave towards more positive potentials indicates that follow-up chemical reaction shift the position of redox equilibrium (1) to the right i.e. to formation of electroinactive product, P. Thus, for high rate constant of the follow-up homogeneous chemical reaction, reverse reoxidation reaction is absent.

Depending on the  $K_c$  value, "limiting" (at  $E_S << E^{0_7}$ ) and maximum currents of forward/cathodic branch of CMP voltammogram

differ from  $\sim 2\%$  to  $\sim 75\%$  for the same voltammogram. Their ratio  $(\Phi_{\rm l}/\Phi_{\rm max})$  was calculated in order to obtain a quantitative parameter for recognition of the electrode mechanism (1). As the limiting current is not well defined for this type of signals, calculations are based on its value at the switching potential (Fig. 2A). As follows from Fig. 3, EC processes can be divided in three groups. The first group includes processes for which the value of limiting to maximum current ratio is approximately one. In such processes the reduction current is insensitive to a follow-up chemical reaction i.e. the effect of the latter (on the net response) is rather small. The third group includes processes in which chemical reaction causes the changed shape of the forward wave and the limiting reduction current is about 25% of the maximum height, both measured on the same CMP voltammogram. Furthermore, the maximum current is about 56% of the limiting current that reflects a simple reversible electrode reaction. In other words, decreasing of the reduction current indicates that there is a depletion of redox components in diffusion layer near the electrode surface as a result of fast chemical conversion, i.e. formation of electroinactive product, P. The second group includes those EC processes in which the influence of follow-up chemical reaction on reduction current is between these two extremes. In such reactions the limiting to maximum current ratio is a linear function of the logarithm of chemical kinetic parameter.

In practice, the influence of chemical reaction on the height, shape and half-wave or peak potential of the voltammetric signal

Table 1 List of symbols

or or symbols.	
$c^*_{Ox}$	Bulk concentration of the reactant of electrode reaction
C <sub>Red</sub>	Concentration of the product of electrode reaction
CP	Concentration of the product of follow-up chemical reaction
D	Common diffusion coefficient
$\Delta E$	Step potential
Ε	Electrode potential
E <sup>0</sup> '	Formal potential
E <sup>0</sup>	Standard potential
Es	Switching potential
Est	Starting potential
$E_1$	"prepulse" (staircase) electrode potential in CDMPV
$E_2$	"pulse" electrode potential in CDMPV
E <sub>SW/DMPV</sub>	Square-wave/differential multipulse amplitude
Ep	Peak potential
f	Square-wave frequency
F	Faraday constant
$\Phi$	Dimensionless current
$arPsi_{ m l}$	Dimensionless limiting reduction current in CMPV
$\Phi_{ m max}$	Dimensionless maximum reduction current in CMPV
$\Phi_1$	Dimensionless "prepulse" component of net current in CDMPV
$\Phi_2$	Dimensionless "pulse" component of net current in CDMPV
$arPhi_{ m f}$	Dimensionless forward component of net current in CSWV
$arPsi_{b}$	Dimensionless backward component of net current in CSWV
$\Delta \Phi_{ m p}$	Dimensionless net peak current
i	Current
i <sub>l,c/a</sub>	Limiting cathodic/anodic current
$\Delta i$	Net current
$k_{\rm f}$	First-order rate constant of the follow-up chemical reaction
$k_{\rm f,r}$	Second-order rate constant of the follow-up chemical reaction
Kc	Dimensionless chemical kinetic parameter
n	Number of electrons
R	Gas constant
S	Electrode surface area
Т	Absolute temperature
t	Time
tp	Pulse time
t <sub>d</sub>	Interval time
τ	Time between pulses
$\Delta t$	Time increment
$\Delta x$	Space increment

can generally be studied by changing the time scale of experiment. In CMP voltammetry this means by changing the pulse duration,  $t_p$ . In other words, if such a (linear) dependence is experimentally obtained for e.g.  $-2 < \log t_p < -1$ , it means that  $-5 < \log K_c < -1$ , assuming that other parameters are the same as in Fig. 2. From this result, it follows a rough estimation of the rate constant of the following chemical reaction, i.e.  $-3 < \log k_f < 0$ . A better assessment of the value  $k_f$  can be achieved by combination of data from all three cyclic multipulse voltammetric techniques (as described in the following paragraphs).

#### 3.2. Cyclic differential multi pulse voltammetry (CDMPV)

The effect of chemical kinetics of electrode reaction (1) (taking place at a planar electrode), on the shape of theoretical cyclic differential multipulse voltammogram, net peak currents and their ratio is presented in Figs. 4–6. The influence of dimensionless chemical kinetic parameter ( $K_c = k_f t_p$ ) was investigated for the following set of standard parameters:  $t_d = 0.15$  s,  $t_p = 25$  ms, n = 1,  $E_{\text{DMPV}} = 50$  mV,  $\Delta E = 2$  mV,  $E_{\text{st}} = 0.6$  V vs.  $E^0$ ,  $E_{\text{s}} = -0.6$  vs.  $E^0$ . Absolute values of cathodic and anodic peak currents (as well as their ratio  $|\Delta \Phi_{\text{p,c}}| \Delta \Phi_{\text{p,c}}|$ ) decrease with the increasing value of the parameter  $K_c$ . To some extent the results are similar to those already discussed in paragraphs about cyclic multi pulse voltammetry. The reverse peak of the CDMP voltammogram completely disappears for the values of  $K_c \ge 10^{-2}$  (Figs. 4 and 5), i.e. for  $k_f \ge 0.4 \text{ s}^{-1}$  if  $t_p = 25$  ms. Accordingly,  $|\Delta \Phi_{\text{p,c}}| < 1$  indicates decreased surface concentration of Red as a result of formation of



**Fig. 2.** (A) Influence of the dimensionless chemical kinetic parameter,  $K_c$ , on theoretical cyclic multipulse voltammograms for electrode reaction (1).  $E_{st} = 0.4 \text{ V}$  vs.  $E^0$ ,  $E_s = -0.4 \text{ V}$  vs.  $E^0$ , n = 1,  $t_d = 0.4 \text{ s}$ ,  $t_p = 50 \text{ ms}$ ,  $\Delta E = 2 \text{ mV}$ ,  $K_c$  (in the descending order) = 0,  $1 \times 10^{-6}$ ,  $5 \times 10^{-6}$ ,  $1 \times 10^{-5}$ ,  $5 \times 10^{-5}$ ,  $1 \times 10^{-4}$ ,  $1 \times 10^{-3}$ , 0.01, 0.1, 0.3, 0.4. Inset: influence of the  $K_c$  value on cyclic staircase voltammograms (for  $K_c = 0.1$  and 0.4). (B) Theoretical dependence of the reduction ( $\blacklozenge$ ) and oxidation ( $\blacktriangle$ ) limiting currents, and their ratio ( $\blacklozenge$ ) on the logarithm of chemical kinetic parameter.



**Fig. 3.** Dependence of the ratio between dimensionless limiting and maximum reduction currents on the logarithm of chemical kinetic parameter, along with CMP voltammograms for  $K_c = 1 \times 10^{-6}$  (a),  $1 \times 10^{-3}$  (b) and 0.4 (c). All other parameters are as in Fig. 2.

product *P*, i.e. indicates the *EC* mechanism. Additionally, increasing the value of parameter  $K_c$  from 0 (which corresponds to a simple reversible electrode reaction) to 0.35 (corresponding to the highest influence of the homogeneous chemical reaction), causes a shift of the cathodic peak potential for 71 mV toward more positive values. This is similar to the shift of cathodic wave in CMPV, and in



**Fig. 4.** Influence of the dimensionless chemical kinetic parameter,  $K_c$ , on the cyclic differential multipulse voltammograms and (pulse ( $\Phi_2$ ) and prepulse ( $\Phi_1$ )) components of their net currents, for electrode reaction (1).  $E_{st} = 0.6$  V vs.  $E^0$ ,  $E_s = -0.6$  V vs.  $E^0$ ,  $t_d = 0.15$  s,  $t_p = 25$  ms, n = 1,  $\Delta E = 2$  mV,  $E_{DMPV} = 50$  mV. Arrows indicate direction of the increase values of parameter  $K_c = 0$  (I),  $1 \times 10^{-5}$ ,  $1 \times 10^{-4}$ ,  $1 \times 10^{-3}$  (II), 0.01, 0.1, 0.35 (III).



**Fig. 5.** Theoretical dependence of the reduction  $(\bullet)$  and oxidation  $(\blacktriangle)$  peak currents of the net CDMPV response, and their ratio  $(\bullet)$ , on the logarithm of chemical kinetic parameter. All other parameters are as in Fig. 4.

accordance with results from Ref. [4]. Another comparison with CMPV clearly indicates that the shape of CDMPV reduction signal is not (very) sensitive to the value of  $K_c$ . Instead of visible changes, described in previous paragraphs, only slight decrease in the halfpeak width could be detected.

Under the highest influence of the chemical reaction, i.e. for  $K_c = 0.35$ , the reduction peak current is about 45% of the current of a simple reversible redox reaction. This decrease of 55% could be attributed to the influence of follow-up chemical reaction on concentration gradient of redox components in diffusion layer. Moreover, during the reverse/anodic potential scan, if  $K_c = 0.35$  (corresponding to  $k_f = 14 \text{ s}^{-1}$  if  $t_p = 25 \text{ ms}$ ), reoxidation Red  $\rightarrow$  Ox is absent. This conclusion arises when components of the net current (see inset in Fig. 4) are analyzed. Under applied conditions, pulse component ( $\Phi_2$ ) is generally very similar to the net response, i.e. its peak on the reverse branch of cyclic signal is not developed



**Fig. 6.** Dependence of the normalized reduction ( $\bullet$ ) and oxidation ( $\blacktriangle$ ) net peak currents of the CDMPV response on  $t_p^{-1/2}$ , for different values of the rate constant of the following chemical reaction:  $k_f/s^{-1} = 0$  (1), 0.002 (2) and 12 (3).

for  $K_c > 10^{-3}$ . Prepulse component ( $\Phi_1$ ) is of minor importance here, but its role could be modified by changing the values of timing and/or potential parameters. Under the extreme conditions, its peak on the reverse branch of current disappears too, but instead of the horizontal line, a small sigmoidal signal appears. Possible application of individual components as diagnostic tools in the analysis of cyclic differential (multi)pulse voltammograms will be treated elsewhere in more detail. Anyway, by analysis of the CDMPV net response and its components the insight into mechanism and kinetics of the electrode reaction becomes possible. More exactly, the rate constant of follow-up chemical reaction can be determined by variation of the pulse duration (as in CMPV). In other words, experimental variation of the chemical kinetic parameter  $K_c$  can be achieved by changing the pulse duration,  $t_p$ , whereas the results are usually presented by plotting the peak current ratio



Scheme 1. An example of estimation of the rate constant of subsequent chemical reaction using cyclic multipulse voltammetric techniques.



**Fig. 7.** Influence of the dimensionless chemical kinetic parameter,  $K_c$ , on net CSWV response (and inset: forward ( $\Phi_f$ ) and backward ( $\Phi_b$ ) components of net current), for electrode reaction (1).  $E_{st} = 0.3$  V vs.  $E^0$ ,  $R_s = -0.3$  V vs.  $E^0$ , n = 1,  $\Delta E = 2$  mV,  $E_{SWV} = 50$  mV. Arrows indicate direction of the increase values of parameter  $K_c = 0$  (I),  $1 \times 10^{-5}$ ,  $1 \times 10^{-4}$ ,  $1 \times 10^{-3}$ , 0.01 (II), 0.1, 0.35 (III).

 $(\Delta i_{p,a}/\Delta i_{p,c})$  in dependence of the logarithm of pulse duration. If the experimentally obtained  $|\Delta i_{p,a}/\Delta i_{p,c}| > 0.1$  for  $\log t_p < -1$ , it follows that  $\log K_c < -3$  (see Fig. 5) and  $\log k_f < -2$ . From these results and the values obtained by CMP voltammetry  $(-3 < \log k_f < 0)$ , it follows that  $-3 < \log k_f < -2$  (Scheme 1). Another possibility for determination of the  $k_f$  value arises from the horizontal part of the current ratio vs.  $\log t_p$  plot in Fig. 5. If experimentally obtained  $|\Delta i_{p,a}/\Delta i_{p,c}|$  is lower than 0.1, i.e. nearly constant for all pulses longer than 0.01 s (i.e. for  $\log t_p > -2$ ) it means that  $\log K_c > -3$  and

 $\log k_f > -1$ , or more precisely (combining the values obtained by CMPV and CDMPV)  $-1 < \log k_f < 0$ .

From this analysis, it is evident that the data obtained using two cyclic multipulse voltammetric techniques provide more information about kinetics of a follow-up chemical reaction, than data obtained applying only one technique.

Fig. 6 shows dependences of the normalized cathodic and anodic peak currents of the net CDMP voltammogram on  $t_p^{-1/2}$ , for a simple reversible electrode reaction ( $k_f/s^{-1} = 0$ ) and for two values



**Fig. 8.** Theoretical dependence of the reduction  $(\bullet)$  and oxidation  $(\blacktriangle)$  net peak currents of the CSWV response, and their ratio  $(\bullet)$ , on the logarithm of chemical kinetic parameter. All other parameters are as in Fig. 7.

of the rate constant of a subsequent chemical reaction:  $k_f/s^{-1} = 0.002$  and 12. It can be seen that the "virtual" slopes of straight lines decrease as the rate constant of a chemical reaction increases. This indicates a reduced influence of timing parameter  $t_p$  on CDMP voltammogram, compared with a simple reversible electrode reaction. Further, the reduced values of the net peak currents indicate decrease concentrations of redox components near the electrode surface as a consequence of the following chemical reaction. All dependencies of the normalized anodic peak currents of the net CDMP voltammogram on  $t_p^{-1/2}$  are linear and pass through the origin, except for an *EC* process for which the value of  $k_f = 0.002 \text{ s}^{-1}$ . The reason for this remains unclear at this time, i.e. possible explanations are not known.

# 3.3. Cyclic square-wave voltammetry (CSWV)

The theoretical influence of dimensionless chemical kinetic parameter  $(K_c = k_f (2f)^{-1})$  on cyclic square-wave voltammograms was investigated for the following set of standard parameters:  $E_{SW} = 50 \text{ mV}, \ \Delta E = 2 \text{ mV}, \ n = 1, \ E_{st} = 0.3 \text{ V vs. } E^0, \ E_s = -0.3 \text{ vs. } E^0.$ Fig. 7 shows the net CSWV responses of reaction (1) for different values of the parameter  $K_c$ . Each cyclic voltammogram consists of one cathodic peak in forward and one anodic peak in reverse scan direction (as in the case of simple reversible redox reaction). However, under the influence of a following chemical reaction absolute values of the net peak currents (and their ratio  $\Delta \Phi_{\rm p,a}/\Delta \Phi_{\rm p,c}$ ) decrease, with complete disappearance of reverse/reoxidation peak of the net CSWV response for  $K_c > 10^{-2}$ . Accordingly, the reverse branch of CSW voltammogram gives the information about stability of the product of redox reaction, Red, in the same way as in previous techniques. Furthermore, additional confirmation of the *EC* mechanism (for  $K_c \ge 10^{-2}$ ) is disappearance of "minimum" of  $\Phi_{\rm b}$  (oxidation) and "maximum" of  $\Phi_{\rm f}$  (reoxidation) current components in cathodic/forward and anodic/reverse scan directions, respectively (see inset in Fig. 7). By increasing the value of this parameter from 0 to 0.35 the reduction peak is shifted for 88 mV towards more positive values. This is almost 20 mV more compared with CDMPV and the greater additional impact of the following chemical reaction on reduction potential in CSWV. Moreover, under the highest influence of a chemical reaction (i.e. for  $K_c = 0.35$  which correspond to  $k_f = 70 \text{ s}^{-1}$  if  $f = 100 \text{ s}^{-1}$ ), the reduction peak current is about 30% of the current of a simple reversible redox process. The decrease of 70% is attributed to the influence of follow-up chemical reaction on the concentration gradient of redox components in diffusion layer (same as in CDMPV). These observations are in accordance with those given in Ref. [10].



**Fig. 9.** Dependence of the net CSWV peak current ratio on the logarithm of squarewave frequency for two values of the rate constant of the following chemical reaction:  $k_f/s^{-1} = 0.003$  (1) and 0.5 (2). All other parameters are as in Fig. 7.

Fig. 8 shows the relationships between the net peak currents (and their ratio) of CSW voltammogram and the logarithm of chemical kinetic parameter. For  $-4.7 \leq \log K_c \leq -3.5$  these relationships are linear:  $\Delta \Phi_{\rm p,c} = -0.497 + 0.051 \cdot \log(K_c)$ ,  $\Delta \Phi_{\rm p,a} = -1.027 - 0.358 \cdot \log(K_c)$  and  $-\frac{\Delta \Phi_{\rm p,a}}{\Delta \Phi_{\rm p,c}} = 1.284 + 0.463 \cdot \log(K_c)$ . Considering that the  $K_c$  is a function of SW frequency and the rate constant of a chemical reaction, in real system experimental dependence of the ratio  $\Delta i_{\rm p,a}/\Delta i_{\rm p,c}$  on  $\log(f)$  can be displayed (Fig. 9). Hence, from the slope of linear dependence the value of  $k_{\rm f}$  could be estimated. More exactly, Fig. 8 shows that  $\Delta \Phi_{\rm p,a}/\Delta \Phi_{\rm p,c}$  depends linearly on the frequency if  $-4.7 < \log K_c < -3.5$ , i.e. this condition determines the values of SW frequencies for above estimated rate constants (obtained by CMP and CDMP voltammetry). So, if we assume (in the first case) that  $-1 < \log k_{\rm f} < 0$ , then for  $1.3 < \log f < 2.5$  (i.e. for  $20 < f/s^{-1} < 316$ ) the linear dependence of  $\Delta i_{\rm p,a}/\Delta i_{\rm p,c}$  must be obtained (see Fig. 9, blue<sup>1</sup> points).

On the other hand, if  $-3 < \log k_{\rm f} < -2$ , it follows that  $-0.7 < \log f < 0.5$  ( $f < 3 \, {\rm s}^{-1}$ ) i.e. no linear dependence of  $\Delta i_{\rm p,a}/\Delta i_{\rm p,c}$  on frequency can be expected (Fig. 9, red<sup>1</sup> points) (Scheme 1).

#### 4. Conclusion

The signals that arise from the application of cyclic multi pulse voltammetry, cyclic differential multi pulse voltammetry and cyclic square-wave voltammetry, for electrode process followed by homogeneous chemical reaction at planar electrode, were simulated. The criteria for recognition of EC mechanism are given:  $|\Phi_{l,a}/\Phi_{l,c}|$  (or  $|\Delta \Phi_{p,a}/\Delta \Phi_{p,c}|$ ) < 1, with complete disappearance of reverse/anodic peak/wave of the net cyclic multipulse voltammogram for  $K_c > 10^{-2}$ . It was shown that follow-up chemical reaction changes the shape (from wave to peak) and position of CMPV signal, compared to a simple reversible electrode reaction (i.e. E mechanism). Furthermore, a new approach to assessment of the rate constant of follow-up chemical reaction, using cyclic multipulse voltammetric techniques, is given as well. According to the values of  $\Phi_{l,c}/\Phi_{max,c}$  ratio (in CMPV), EC processes can be divided in three groups. One of them includes those EC processes for which this currents ratio is a linear function of the logarithm of chemical kinetic parameter,  $K_c$  (where  $K_c = k_f t_p$ ). Accordingly, the rate constant of follow-up chemical reaction can be determined by

 $<sup>^{1}\,</sup>$  For interpretation of color in Fig. 9, the reader is referred to the web version of this article.

the variation of pulse duration (in CMPV and CDMPV) or frequency (in CSWV).

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