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SURFACE CATALYTIC MECHANISM: THEORETICAL STUDY UNDER CONDITIONS OF DIFFERENTIAL SQUARE-WAVE VOLTAMMETRY*

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Differential square-wave voltammetry (DSWV) is the most recent modification of square-wave voltammetry (SWV), developed to advance the performance of the technique for both analytical and kinetic applications. The differential current-measuring protocol in DSWV leads to improved voltammetric features of the forward and backward current components, particularly when slow, *i.e.*, quasireversible or irreversible electrode reactions are studied. In the present theoretical work, the catalytic electrode mechanism of the surface bound redox species (surface EC′ mechanism) is studied under the conditions of the new technique, where E denotes the electrode reaction and C′ refers to the irreversible follow-up regenerative chemical reaction. The theoretical data presented provides a general overview of the EC′ reaction scheme, implying some specific voltammetric features that can be exploited for the estimation of relevant physical parameters of the electrode reaction E and the regenerative chemical reaction C′.

Keywords: differential square-wave voltammetry; surface catalytic mechanism;
enzyme-substrate interactions; quasireversible maximum; protein-film voltammetry

ПОВРШИНСКИ КАТАЛИТИЧКИ МЕХАНИЗАМ: ТЕОРЕТСКА СТУДИЈА ВО УСЛОВИ НА ДИФЕРЕНЦИЈАЛНА КВАДРАТНО-БРАНОВА ВОЛТАМЕТРИЈА

Диференцијалната квадратно-бранова волтаметрија (DSWV) е неодамнешна модификација на техниката квадратно-бранова волтаметрија (SWV), што е развиена со цел да се подобрат нејзините перформанси како за аналитички така и за кинетички апликации. Диференцијалниот протокол на мерењето на струјата во DSWV придонесува за подобрување на својствата на волтаметриските криви на директните и повратните струјни компоненти, посебно во случаи на бавни, т.е. квазиреверзибилни или иреверзибилни електродни реакции. Во овој теоретски труд е студиран каталитичкиот површински електроден механизам (површински EC′-механизам) во услови на новата техника DSWV, каде што E означува електродна реакција, додека C′ се однесува на иреверзибилна последователна регенеративна хемиска реакција. Презентираните теоретски резултати даваат целосен преглед на површинскиот EC′-механизам, при што е покажано дека одредени специфични својства на овој механизам можат да се употребат за определување на релевантни физички параметри кај електродната реакција E и кај регенеративната хемиска реакција C′.

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[*] We dedicate this work to our great teacher and great friend, Dr. Milivoj Lovrić (Croatia), on the occasion of his 70th birthday

Клучни зборови: диференцијална квадратно-бранова волтаметрија; површински-каталитички механизам; ензимско-супстратни интеракции; квазиреверзибилен максимум; волтаметрија на тенок протеински слој

1. INTRODUCTION

Various processes for mass and/or energy conversion in biochemistry and chemical technology require the action of a catalyst, in order to be accelerated and to proceed with an effective rate, which compels a permanent need to study the kinetics of these intrinsically important processes. With regard to biochemical reactions, though many enzymes are classified as specific catalysts, with a known function, there are significant ongoing efforts to evaluate their mechanism and the kinetics of action. Indeed, electrochemical techniques are among the most relevant methods to study the activity of many enzymes and redox active proteins.[1] Recent electrochemical studies following the methodology of protein-film voltammetry have contributed to the fundamental understanding of the reaction mechanism of important classes of redox enzymes.[2–4]

Under idealized conditions, voltammetric techniques can be used to evaluate the ongoing catalytic mechanism, affording information on the activity of the catalyst, and probing the magnitude of the catalytic rate constant.[5–7] There are several methods reported to accurately and appropriately extract kinetic parameters from a set of voltammetric data.[2–5,8–10] Indeed, the features of the so-called "electrochemical regenerative" (sometimes named as the "electrocatalytic mechanism", or simply the "EC′ mechanism") provide the basis with which to study electroactive enzymes and to estimate the kinetics of the enzyme-substrate reaction.[1–8,10] Commonly, cyclic voltammetry (CV) is applied for the mechanistic and kinetic characterization of enzyme-substrate interactions.[3,4,6,7,10] With the progressively increasing application of square-wave voltammetry (SWV),[11,12] substantial development has occurred in the field of enzyme-substrate reaction kinetics in recent decades. Several simple and efficient SW voltammetric methods for the determination of enzyme kinetics are based upon the EC′ mechanism.[5,13–16]

It is well-known that the introduction of pulse voltammetric techniques, where SWV is recognized as one of the most advanced members, into electroanalytical chemistry was motivated by the need to minimize the contribution of the capacitance current measured in the course of a voltammetric experiment, and thus to increase the analytical sensitivity.[8,11,12] The potential modulation of SWV consists of a series of symmetrical square-wave pulses, which are superimposed on a staircase potential ramp. The current sampling procedure occurs twice within a SW potential cycle that comprises two adjacent pulses; in other words, it is carried out in a small time-segment at the end of each forward and reverse pulse. If, for instance, the currents measured at the forward pulses (*i.e.*, forward current) are due to oxidation of the electroactive species, the currents measured in the reverse pulses (reverse current) give rise to the reduction current. In addition, a net current component can be defined, and is obtained as a difference between the forward and reverse current. As elaborated in the studies by Osteryoung[11] and Mirceski, Komorsky-Lovric and Lovric,[12] SWV is a very rapid and sensitive technique. However, when kinetically sluggish electrode processes are encountered, which is actually the most frequent experimental case, the technique fails to provide reliable kinetic data.[11,12]

In order to improve the overall performance of SWV, a slight modification has recently been proposed, resulting in a new voltammetric technique termed differential square-wave voltammetry (DSWV).[15] This technique can be considered as a hybrid form of differential pulse voltammetry (DPV) and SWV (Fig. 1). The main difference compared to the conventional SWV (Fig. 1B) is seen in the insertion of an additional step potential between each potential cycle, consisting of two adjacent, oppositely oriented potential pulses (Fig. 1C). On the other hand, from the perspective of DPV (Fig. 1A), the modification in the new technique is seen in the insertion of a reverse potential pulse, adjacent to each forward pulse of the conventional DPV. In the new technique, the current is measured at the end of the potential step and the two potential pulses (Fig. 1D). Thus, by calculating the difference between the “pulse-currents” (I_f and I_r) and the "step current" (I_s), the differential forward and reverse SW voltammetric components can be obtained (see Fig. 1D). Such a current sampling procedure and presentation of the data in DSWV significantly affects the features of the voltammetric patterns, in particular when slow electrode processes are considered,[17] or when the electrode reaction is coupled with a fast chemical reaction, as demonstrated in the present study.

Hence, in this work, the features of the surface regenerative EC′ reaction scheme, as one of the most important electrode mechanisms in voltammetry, are theoretically studied under conditions of DSWV. The majority of the voltammetric data obtained by means of numerical simulations are compared to the voltammetric outcome under conditions of conventional SWV.[8,9,11,13,14,16]

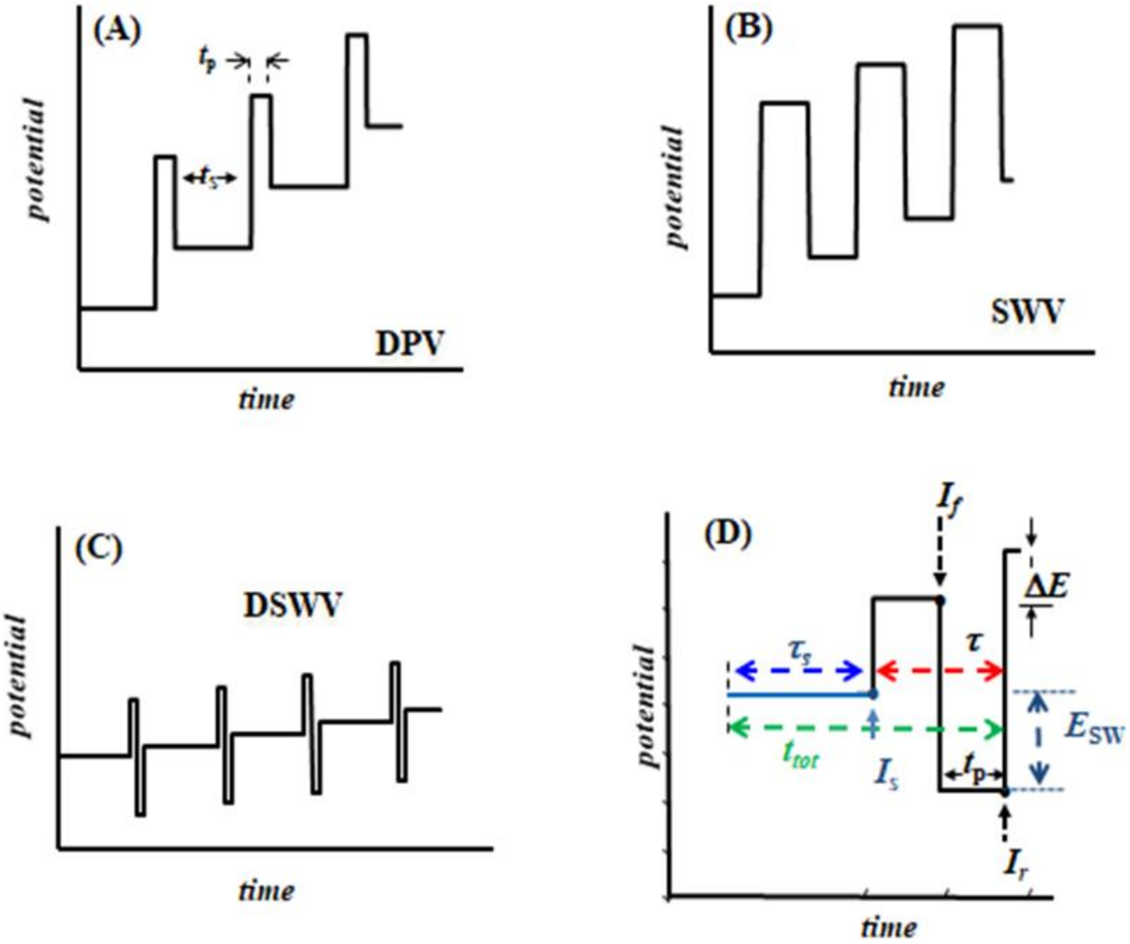

Fig. 1. Potential modulation in **(A)** differential pulse voltammetry (DPV); **(B)** square-wave voltammetry (SWV); and **(C)** differential square-wave voltammetry (DSWV). Panel **(D)** displays characteristic parameters of a single potential cycle in DSWV: the duration of two adjacent potential pulses is assigned with τ, while t_p stays for the duration of single pulse; τ_s is the symbol for the time duration of the potential step preceding the two potential pulses; with E_{sw} the height of the pulses (i.e., the SW amplitude) is assigned, while ΔE is the symbol for the step potential. I_s, I_f, and I_r, refer to the sampling points were current is measured at the end of the potential step (I_s), the forward pulse (I_f), and the reverse pulse (I_r). The most notable feature of the technique is that differential forward and reverse current components can be defined as $I_{f,\,diff} = I_f – I_s$, and $I_{r,diff} = I_r - I_s$.

2. AN OUTLINE OF THE MATHEMATICAL MODEL AND SIMULATION PROCEDURE

The surface confined electrocatalytic (regenerative) electrode mechanism (surface EC′) is described using the following scheme, where the charge of the species is omitted for the sake of simplicity:

$$\mathrm{Ox(ads)} + n\mathrm{e} \overset{k_s}{\rightleftarrows} \mathrm{Red(ads)} \qquad \mathrm{E}$$

$$\mathrm{Red(ads)} + \mathrm{Y(sol)} \xrightarrow{k_c'} \mathrm{Ox(ads)} \qquad \mathrm{C'}$$

It is assumed that both electroactive species (Ox and Red) are strongly immobilized on the electrode surface, and there is no additional mass transport in the course of the voltammetric experiment. It is also assumed that a uniform layer is formed on the working electrode surface, with no lateral interactions between immobilized electroactive species. The symbol "Y(sol)" is assigned to electrochemically inactive, yet redox active, dissolved species present in a large excess in the system. Consequently, the concentration of the substrate $c^*(\mathrm{Y})$ is virtually constant at the electrode surface in the course of the voltammetric experiment, and the redox chemical step C′ is of pseudo first-order in terms of the chemical kinetics, characterized with the first order rate constant $k_c = k_c'c^*(\mathrm{Y})$. Moreover, the substrate Y(sol) is assumed to react selectively with the electroactive form Red in a chemically irreversible manner. The mathematical representation of the studied mechanism under pulse voltammetric conditions is given elsewhere.[12,16] The working protocol in the MATHCAD software package that enables simulation of the voltammetric outcome under conditions of DSWV is provided in the Supplementary material.

Briefly, the recurrent formula for calculating the dimensionless current Ψ as a function of the applied potential and other kinetic parameters is given with the following equation (1):

$$\Psi_{\mathrm{m}} = \frac{\mathrm{K_{ET}}\, \mathrm{e}^{-\alpha\Phi\mathrm{m}}\left(1 - \frac{1+\mathrm{e}^{\Phi\mathrm{m}}}{\mathrm{K_{cat}}}\right)\sum_{j=1}^{j-1}\Psi_{\mathrm{j}}\mathrm{M}_{\mathrm{m-j+1}}}{1 + \mathrm{K_{ET}}\, \mathrm{e}^{-\alpha\Phi\mathrm{m}}\left(1 + \frac{\mathrm{e}^{\Phi\mathrm{m}}\mathrm{M}_1}{\mathrm{K_{cat}}}\right)} \qquad (1),$$

which is derived by assuming that the reduction current is positive, based on the Butler-Volmer kinetic equation. The dimensionless current is defined as $\Psi = I/[(nFSf\Gamma^*)]$, where I is for the electric current, n is the stoichiometric number of electrons, F is the Faraday constant, S is the active surface area of the working electrode, and f is the frequency of potential pulses, which is related to the duration of a potential pulse t_p as $f = 1/(2t_p)$ (see Fig. 1D). In addition, Γ^* is the total surface concentration, being identical to the initial surface concentration of the electroactive form Ox(ads). Φ is the dimensionless potential, defined as $\Phi = \frac{nF}{RT}\left(E - E^{\phi\prime}\right)$, where $E^{\phi\prime}$ is the formal redox potential, α is the cathodic electron transfer coefficient according to the Butler-Volmer formalism in eq. (1), R is universal gas constant, and T is the thermodynamic temperature.

The symbol K_{ET} refers to the dimensionless electrode kinetic parameter, defined as $K_{\mathrm{ET}} = k_s/f$, which relates to the formal rate constant of the electrode reaction k_s (s^{-1}) to the frequency of potential pulses. As is typical for the surface EC′ mechanism, the dimensionless chemical kinetic parameter is defined as $K_{\mathrm{cat}} = k_c/f$.[16] In addition, M is a numerical integration factor, defined as $M_m = \exp[-K_{\mathrm{cat}}(m-1)/50)] - \exp[-K_{\mathrm{cat}}m/50]$, where m is the serial number of time increments. At this stage, it is worth mentioning that DSWV is characterized with a parameter termed the step-to-pulse duration ratio $r = \tau_s/t_p$, which represents the role of the potential step τ_s, relative to the duration of the pulses t_p (see Fig. 1D). The step-to-pulse duration ratio is a new parameter for DSWV, in comparison with conventional SWV.[15]

Theoretical data are mainly presented in the form of dimensionless differential forward and reverse current components, calculated as $\Psi_{\mathrm{f,diff}} = \Psi_{\mathrm{f}} - \Psi_{\mathrm{s}}$ and $\Psi_{\mathrm{r,diff}} = \Psi_{\mathrm{r}} - \Psi_{\mathrm{s}}$, respectively, (Fig. 1D),[15] where Ψ_{f} and Ψ_{r} are the forward and reverse currents measured at the end of the pulses. Thus, the unique characteristic of DSWV is that all three current components, $\Psi_{\mathrm{f,diff}}$, $\Psi_{\mathrm{r,diff}}$, and the net component ($\Psi_{\mathrm{net}} = \Psi_{\mathrm{f}} - \Psi_{\mathrm{r}}$) have a differential nature.

3. RESULTS AND DISCUSSION

The outcome of the virtual experiment under conditions of DSWV depends predominantly on the dimensionless electrode kinetic parameter K_{ET} and the catalytic parameter K_{cat}. For $K_{\mathrm{cat}} \le 10^{-3}$, the electrode mechanism simplifies to a common surface electrode reaction, and the role of the catalytic regeneration is insignificant for any value of K_{ET}. Under such conditions, the role of the step-to-pulse duration ratio $r = \tau_s/t_p$ is significant for slow electrode reactions, attributed approximately with $K_{\mathrm{ET}} < 0.5$, *i.e.*, sluggish quasireversible and irreversible reactions. Figure 2 illustrates the effect of r to the evolution of the voltammetric response, considering the common forward (Ψ_{f}), reverse (Ψ_{r}) and net (Ψ_{net}) components.

For a given value of K_{ET}, the apparent electrochemical reversibility of the electrode reaction increases in proportion to r, being in agreement with previous findings.[15] Thus, generally speaking, the DSWV can access slower electrode reactions rather than conventional SWV, as the overall scan rate of the voltammetric experiment decreases by increasing r, *i.e.*, by extending the duration of the step potential. For faster electrode reactions (roughly, for $K_{\mathrm{ET}} \ge 1$), the role of r is insignificant, while the features of the voltammetric response depend solely on the dimensionless parameters K_{ET} and K_{cat}. Under such conditions, the electrode reaction is sufficiently fast to enable the redox species to virtually accommodate at redox equilibrium at the end of the step; hence, the voltammetric outcome is predominantly controlled by the parameters K_{ET} and K_{cat}, as well as the height of the potential pulses, *i.e.*, the SW amplitude (E_{sw}).

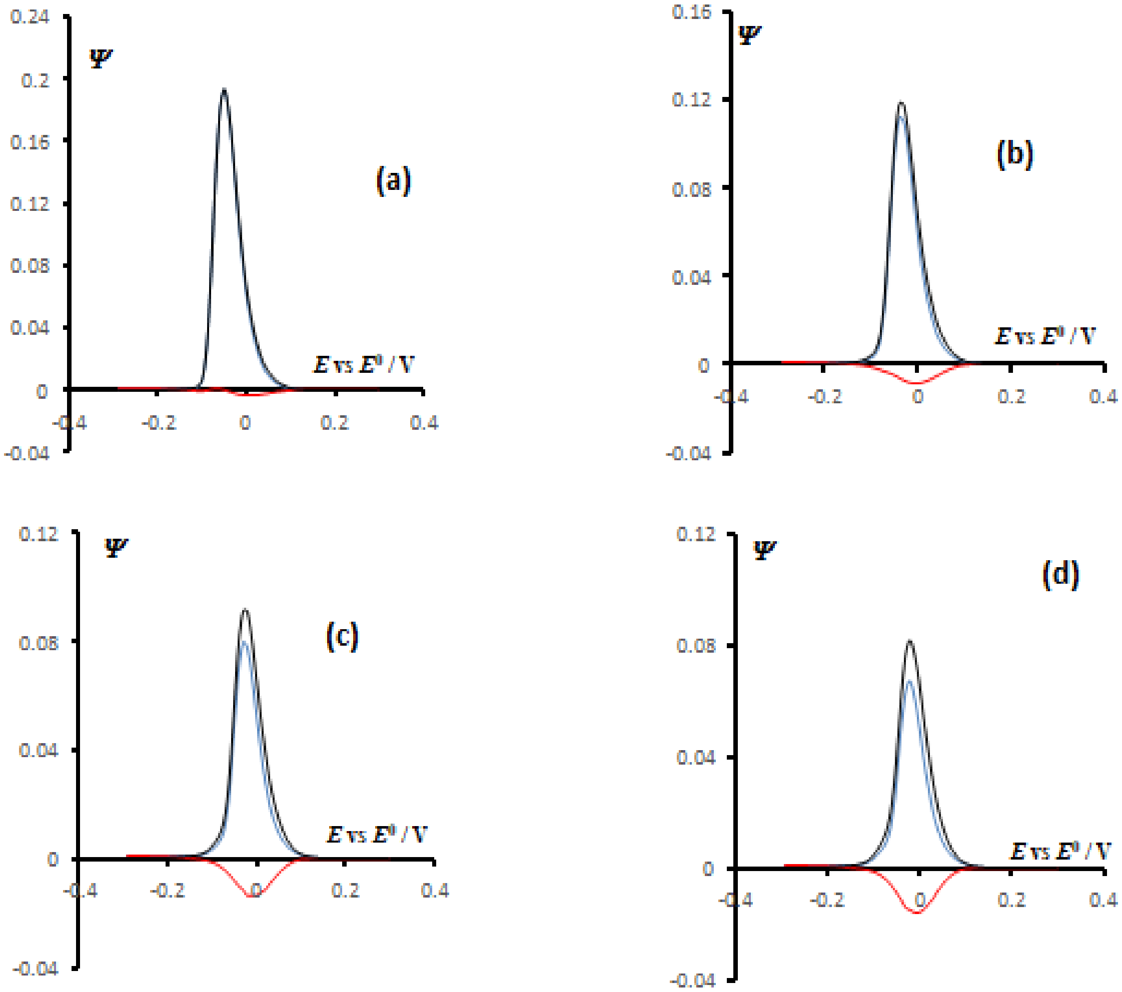

Fig. 2. The effect of the step-to-pulse duration ratio $r = \tau_s/t_p$ on the morphology of the SW forward (Ψ_f, blue line), reverse (Ψ_r, red line), and net component of differential square-wave voltammograms of a sluggish electrode reaction. The value of the ratio is $r = 2$ (**a**); 10 (**b**); 20 (**c**) and 30 (**d**). The other simulation parameters are: electrode kinetic parameter $K_{ET} = 0.01$, catalytic parameter $K_{cat} = 0.001$, electron transfer coefficient $\alpha = 0.5$, stoichiometric number of electrons $n = 2$, SW amplitude $E_{sw} = 50$ mV, step potential increment $\Delta E = 10$ mV, and temperature $T = 298$ K.

Yet, the advantage of DSWV over SWV fully emerges when considering the evolution of differential voltammetric components. Fig. 3 shows a set of representative voltammetric patterns under conditions of DSWV (a-d) and conventional SWV (a′-d′),[16] simulated as a function of the dimensionless catalytic rate parameter K_{cat}. Note that the step-to-pulse duration ratio in DSWV is set to $r = 4$. Another important point to note is that the dimensionless current is defined identically in both techniques, by means of the frequency (f) of the SW pulses ($\Psi = I/[(nFSf\Gamma^*)]$). Thus, the comparison presented in Fig. 3 corresponds to the situation in which the frequency and the rate constants of the electrode and the chemical reaction are identical for both techniques. As expected, the forward and backward voltammetric components in conventional SWV exhibit a characteristic sigmoid shape when the catalytic parameter is large (Figs. 3c′–d′). However, one observes quite different voltammetric profiles under conditions of DSWV. As the rate of the catalytic reaction increases, both differential voltammetric components enlarge simultaneously (Figs. 3b–d), instead of the commonly observed behavior in conventional SWV, where the forward component increases, while the backward one concomitantly decreases (Figs. 3b′–d′). Moreover, a sigmoid shape of the differential forward and backward voltammetric components cannot be obtained for any value of K_{cat}; rather, they are well-defined peaks, with precisely measurable peak parameters.

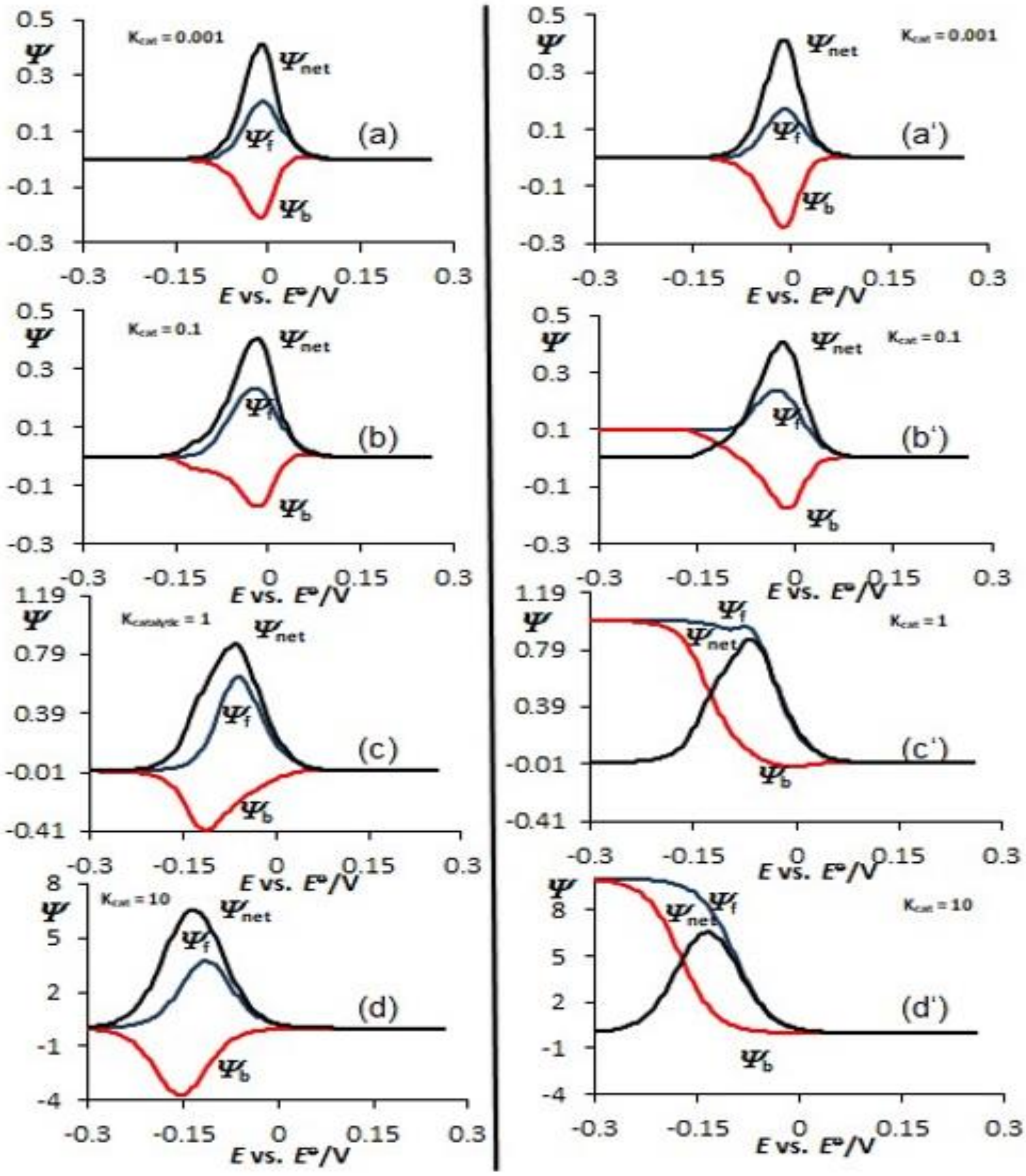

Fig. 3. Differential square-wave voltammograms **(a–d)** and conventional square-wave voltammograms **(a′–d′)** representing the effect of the dimensionless catalytic parameter K_{cat}. All voltammograms are calculated for the electrode kinetic parameter $K_{ET} = 0.1$. For differential square-wave voltammetry (panels a–d) the step-to-pulse duration ratio is $r = 4$. The potential increment used was set to $\Delta E = 4$ mV. Other conditions are same as in Fig. 2.

To comprehend the evolution of the differential components, Fig. 4 displays the step (Ψ_s) and pulse current components (Ψ_f and Ψ_r) obtained for a large rate of the catalytic (regenerative) reaction C′ in DSWV.

Obviously, all non-differential components feature a sigmoid shape (Fig. 4a). Due to the current subtraction procedure, both differential forward and reverse components acquire a well-developed peak-like shape, as shown in Fig. 4b. Thus, the differential forward ($\Psi_{f,diff}$) and reverse ($\Psi_{r,diff}$) voltammetric curves could be understood as a sort of primitive first derivative of the real sigmoid curves (Ψ_f and Ψ_r, respectively). Such a measuring protocol allows the exploration of the features of the forward and backward currents for mechanistic, analytical, and kinetic purposes, even at very large rates of the catalytic reaction. In addition, the voltammetric study can be based on the analysis of the net component in DSWV, similar to conventional SWV.

Figure 5 shows several working curves illustrating the effect of the catalytic parameter K_{cat} to the ratio of the forward-to-reverse peak-currents of the differential voltammetric curves ($\Psi_{f,diff,p}/\Psi_{r,diff,p}$) (a) and their peak-potential separation ($E_{p,f,diff} - E_{p,r,diff}$) (b).

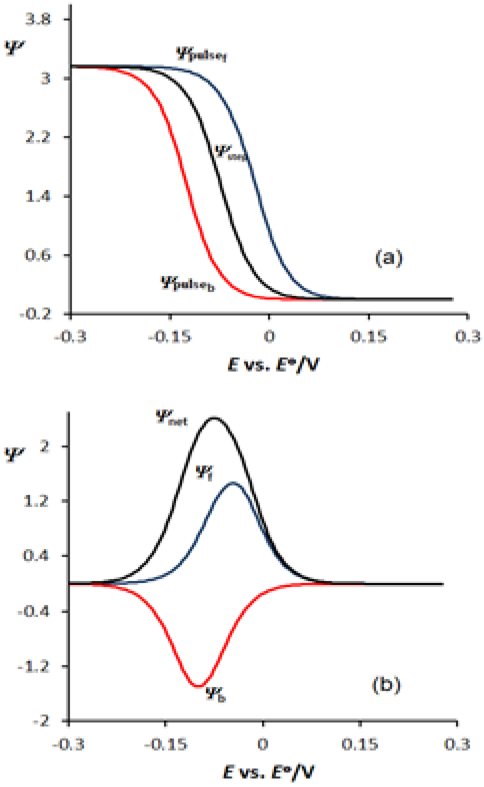

Fig. 4. Representative voltammogram of the EC′ mechanism featuring fast regenerative C′ reaction in DSWV showing forward (Ψ_f), reverse (Ψ_r) and the step-current (Ψ_s) components (**a**), and the corresponding differential forward ($\Psi_{f,diff}$), reverse ($\Psi_{r,\,diff}$) and net-current ($\Psi_{net} = \Psi_{f,diff} - \Psi_{r,diff}$) components (**b**). The simulation conditions are: K_{ET} = 0.18, K_{cat} = 3.16, and ΔE = 4mV. Other conditions are same as in Fig. 2.

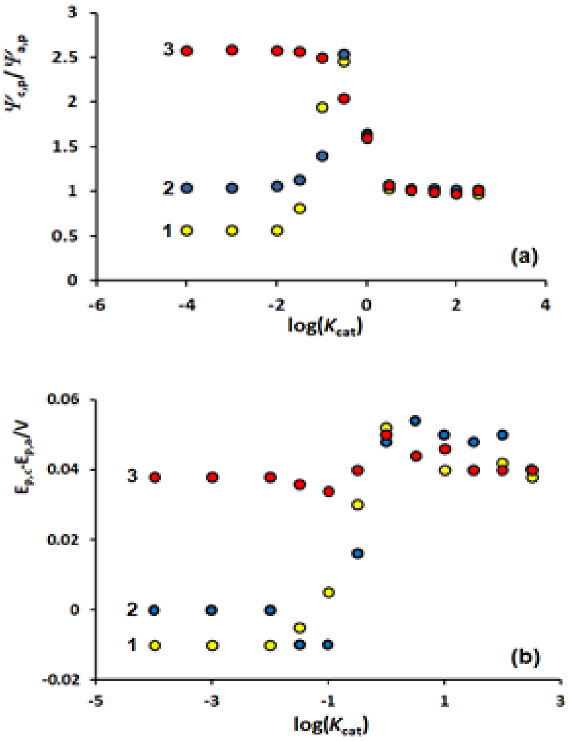

Fig. 5. Dependence of the forward-to-reverse peak-current ratio ($\Psi_{f,diff}/\Psi_{r,diff}$) **(a)** and peak-to-peak potential separations ($E_{p,diff,f} - E_{p,diff,r}$) of differential current components **(b)** as a function of the logarithm of the dimensionless rate catalytic parameter log(K_{cat}). The values of K_{ET} were set to 0.032 (*1*); 0.1 (*2*), and 1 (*3*) for both panels **(a)** and **(b)**. The potential increment in this set of simulations was set to ΔE = 4 mV. Other simulation parameters are same as in Fig. 2.

The peak-current ratio exhibits a parabolic dependence on log(K_{cat}), with the maximum being located close to log(K_{cat}) = –0.5 for a sluggish electrode reaction (curves 1 and 2 in Fig. 5a). For faster electrode reactions, a sigmoid function is observed (curve 3 in Fig. 5a). Such a specific shape of the function ($\Psi_{\mathrm{f,diff,p}}/\Psi_{\mathrm{r,diff,p}}$) *vs.* log($K_{\mathrm{cat}}$) can be exploited to estimate the real catalytic rate k'_{c} by fitting the experimental and theoretical data, provided the standard rate constant is previously know. It should be noted that, in experimental reality, the variation K_{cat} can be carried out by studying a given electrode mechanism at a particular frequency and r of DSWV, by changing the concentration of the substrate c^*(Y), recalling that $K_{\mathrm{cat}} = k_{\mathrm{c}}{'}c^*(\mathrm{Y})/f$. Hence, the theoretical data of Fig. 5 can be readily reproduced experimentally and used for the estimation of $k_{\mathrm{c}}{'}$.

The peak-to-peak potential separation depends sigmoidally on log(K_{cat}), with a linear part found approximately within the region –1 < log(K_{cat}) < 0.5 (Fig. 5b). Recalling that the effect of the catalytic parameter K_{cat} in conventional SWV is obtained by analyzing the net peak-current, which commonly increases monotonically with K_{cat}, while the net peak-potential is unaffected by K_{cat}.[16] Obviously, in DSWV, more voltammetric features are available for kinetic analysis than in conventional SWV.

A typical voltammetric characteristic of all surface electrode mechanisms under conditions of pulse voltammetric techniques is the phenomenon known as "quasireversible maximum". This term refers to the relationship between the dimensionless peak-current and the electrode kinetic parameter, implying that the maximal peak-current is found within the quasireversible kinetic region.[11,12] For instance, as reported by Mirceski, Komorsky-Lovric and Lovric in,[12] for a simple surface electrode reaction, the parabolic dependence of the dimensionless net peak-current as a function of log(K_{ET}) can be explored to estimate the standard rate constant in a simple experimental protocol conducted with conventional SWV. Accordingly, Fig. 6 presents a series of quasireversible maxima of the surface EC′ mechanism, calculated under conditions of DSWV, by varying the dimensionless kinetic parameter K_{ET}. These theoretical data correspond to the comparison of a series of electrode reactions characterized with different K_{ET} and the same catalytic parameter K_{cat}, *i.e.*, the same rate constant of the C′ reaction.

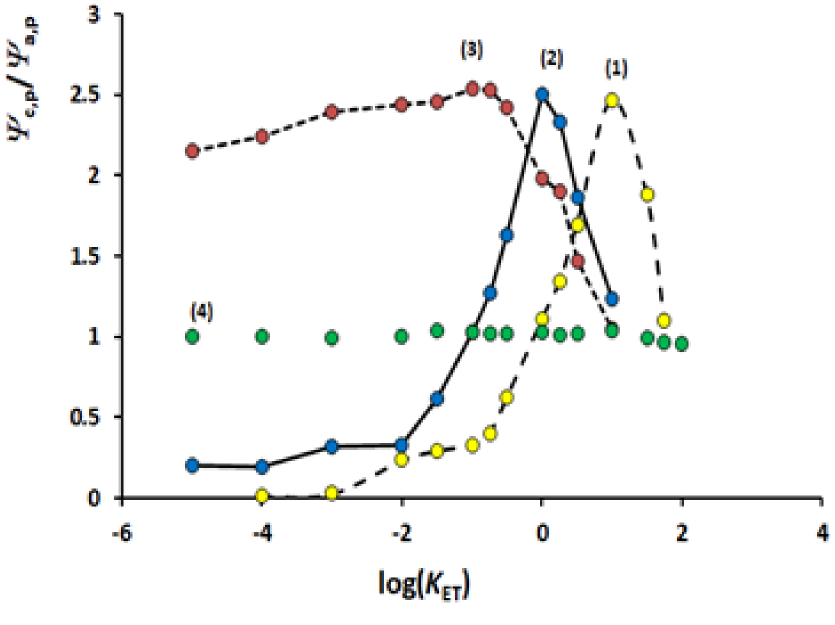

Fig. 6. The dependence of the forward-to-reverse peak-current ratio ($\Psi_{\mathrm{f,diff}}/\Psi_{\mathrm{r,diff}}$) of differential components as a function of logarithm of the dimensionless electrode kinetic parameter log(K_{ET}). The values of the dimensionless catalytic parameter are K_{cat} = 0.01 (*1*); 0.001 (*2*); 0.316 (*3*) and 10 (*4*). The potential increment in this set of simulations was set to ΔE = 4 mV. Other simulation parameters are same as in Fig. 2.

An important note, however, is that the quasireversible maximum is constructed by using the peak-current ratio of the differential forward and backward components instead of the net peak-current, as is commonly used in conventional SWV. The relative character of the parameter

($\varPsi_{\mathrm{f,diff,p}}$ / $\varPsi_{\mathrm{r,diff,p}}$) is highly advantageous, as it enables direct comparison of the theoretical and experimental data. In other words, the theoretically predicted variation of the ratio ($\varPsi_{\mathrm{f,diff,p}}$ / $\varPsi_{\mathrm{r,diff,p}}$) is analogous to the ratio of the real, experimentally-measured currents ($I_{\mathrm{f,diff,p}}$ / $I_{\mathrm{r,diff,p}}$). Importantly, the peak-current ratio cannot be considered in conventional SWV, as the measurement of the peak-current of both forward and backward components is hardly possible when the regenerative chemical reaction is very fast relative to the SW frequency.

The working curves in Figure 6 have been constructed for different rates of the regenerative chemical step. Obviously, the position of quasireversible maximum based on the ratio $\varPsi_{\mathrm{f,diff,p}}$ / $\varPsi_{\mathrm{r,diff,p}}$ is a function of the kinetics of the reaction C′. For moderate rates of the regenerative reaction, the position of the maximum shifts towards lower critical values of K_{ET} by increasing the value of K_{cat} (curves 1–3 in Fig. 6). For larger rates of the catalytic reaction C′, *i.e.*, $\log(K_{\mathrm{cat}}) > 0.25$, the quasireversible maximum vanishes (see curve 4 in Fig. 6).

However, when a single electrode mechanism is studied, which is associated with given values of the rate constants k_{s} and k_{c}, the dimensionless parameters K_{ET} and K_{cat} can be varied by altering the SW frequency. The effect of the frequency is expected to be rather complex, as both dimensionless parameters will be affected simultaneously. Extensive simulations have been performed, corresponding to a real experiment of a single electrode reaction in which the frequency has been varied from 2 to 1000 Hz (data not shown). The general conclusion is that the particular effect of the frequency depends on the ratio between the rate constants k_{c} / k_{s}, as in conventional SWV.[16] Both the dimensionless net peak-current and the differential peak-current ratio depend parabolically on the log(f) with a maximum positioned within the quasireversible kinetic region. The position of the maximum is sensitive to the rate constant of the catalytic reaction C′ if the ratio k_{c} / k_{s} is approximately higher than 0.02, which enables the determination of k_{c}, providing that k_{s} is previously known. Yet, when k_{c} / k_{s} is approximately > 1, the effect of the catalytic reaction C′ prevails, and the quasireversible maximum vanishes, considering either the dimensionless net peak-current or the differential peak-current ratio.

Another characteristic phenomenon of surface electrode mechanisms under SW voltammetric conditions is the "splitting of the net peak".[18] The splitting is typical for all surface electrode processes featuring fast rates of the electrode reaction,[11] which are capable of approaching the redox equilibrium within the time frame of a potential pulse. As a consequence, the reduction peak in conventional SWV shifts toward more positive potentials, while the oxidation peak shifts in the opposite direction as the rate of the electron transfer increases. This, in turn, leads to a split net SW voltammetric peak. Under such conditions, the current measured at the end of the pulses is commonly rather small, resulting in a minute voltammetric response[11,18] consisting of separated forward and reverse components, thus being a split net peak. For instance, for $\log(K_{\mathrm{ET}}) = 0.5$ and $K_{\mathrm{cat}} < 1$, the net peak splits in both techniques (for $E_{\mathrm{SW}} = 50$ mV, $\Delta E = 4$ mV, and $n = 2$; data not shown); over the interval $K_{\mathrm{cat}} > 1$, the splitting vanishes in both techniques, as the forward and reverse current components gain a sigmoid shape in the conventional SWV, while the potential separation of differential components decreases in DSWV.

A brief analysis of the net peak in DSWV has also been carried out as a function of the electron transfer coefficient (α). Simulations have been conducted for a slow, moderate, and fast regenerative catalytic reaction C′, assuming a typical quasireversible electrode reaction associated with $K_{\mathrm{ET}} = 0.5$ (data not shown). The relationship between the peak-potential and the logarithm of the electron transfer coefficient is complex and nonlinear, whereas the peak-current depends linearly on $\log(\alpha)$ for a broad range of rates of the regenerative chemical reaction C′ (*i.e.*, $-3 \le \log(K_{\mathrm{cat}}) \le 2$). A useful approach for the determination of α is to study the peak current ratio of the differential voltammetric components ($\varPsi_{\mathrm{f,diff,p}}/\varPsi_{\mathrm{r,diff,p}}$). The ratio depends linearly on α for $\log(K_{\mathrm{cat}}) \le -1$ over the interval $0.3 \le \alpha \le 0.7$. For instance, for $K_{\mathrm{cat}} = 0.1$, the relationship can be described with the regression line $\varPsi_{\mathrm{f,diff,p}}/\varPsi_{\mathrm{r,diff,p}} = 0.69\alpha + 0.26$ ($R^2 = 0.99$), which is valid for $K_{\mathrm{ET}} = 0.5$, $E_{\mathrm{sw}} = 50$ mV, and dE = 4 mV. The slope and the intercept of the regression line depend on the electrode kinetic parameter, implying that the peak-current ratio can be used to estimate α if the standard rate constant of the electrode reaction is previously known.

Finally, it is worth briefly discussing the effect of the pulse amplitude under conditions of DSWV and SWV. As expected, the pulse amplitude affects all relevant features of voltammograms simulated in both DSWV and SWV. The SW amplitude can be effectively used to study the peak-potential separation of differential forward and reverse voltammetric components, to estimate either the kinetics of both the electrode reaction and the chemical regenerative reaction C′. Moreover, in an analytical context, it is worth noting that the ratio between the peak-current and the half-peak width of the net voltammetric component is recognized as a relevant criterion for selecting the optimal value of the amplitude. For both techniques, such a ratio has a maximal value if the product nE_{sw} is between 40 mV and 60 mV, where n is the stoichiometric number of electrons.

4. CONCLUSIONS

The recent introduction of DSWV resulted from the need to improve the performance of pulse voltammetric techniques for mechanistic, kinetic, and analytical applications. The insertion of a potential step with a defined duration between the SW potential cycles decreases the overall rate of the voltammetric experiment, thus enabling analysis of slower electrode reactions. In parallel, it enables forward and reverse SW voltammetric components to be transformed into differential voltammetric curves with precisely measurable peak characteristics, which expands the basis for in-depth mechanistic and kinetic characterization of a given electrode mechanism. This brief study of the surface EC′ mechanism demonstrates that voltammetric analysis can be carried out in a similar way to conventional SWV, if the net voltammetric component is analyzed. The advantage of DSWV is that slower electrode reactions can be studied by expanding the duration of the step potential, compared to conventional SWV. Moreover, DSWV provides a plethora of additional voltammetric features based on the interrelation of differential forward and reverse voltammetric components, which are directly comparable to the experimental data.

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