Theory of square-wave catalytic adsorptive stripping voltammetry. How to obtain mechanistic information from experimental data

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ABSTRACT

The sensitivity of a catalytic adsorptive stripping voltammetric method depends mainly on the strength of adsorption of the electroactive reactant and the efficiency of the catalytic reaction. While the strength of adsorption is associated with the type of reagent and the solution pH, the efficiency of the catalytic step depends on the type and concentration of the oxidant selected for such reaction. Although the probe-and-error approach is commonly used for optimizing a given analytical signal, information about the reaction scheme and some good estimation about the rate constants of involved reactions would help a lot to optimize the analytical system.

The possibility for using the quasi-reversible maximum to study the electrode kinetics depends on the values of k_{cat}, K_{ad}, f, E_{sw}, and of course k_s. As a result of this, it is rather difficult for experimentalist and also for theoreticians to organize a strategy for detecting and understanding the effect of each variable separately. In this manuscript, it is first shown the effect of different variables on the voltammetric response, and then it is suggested a strategy for studying and estimating the values of those variables. Thus, if the experimental system matches the reaction scheme of an electrochemical reaction complicated by following homogeneous catalytic reaction, then it is advisable to follow a set of simple experimental steps to characterize the kinetic constants of the system.

1. Introduction

Nowadays, adsorptive accumulation has become one of the most used strategies for increasing the sensitivity of diverse electroanalytical methods. This strategy typically involves the application of a suitable potential that favors the adsorption of reagents at the electrode surface [1–6]. Once the electroactive species have been accumulated, a potential scan is applied to detect the analytical signal. The analysis of traces requires the quantification of analytes with very low concentration values, in which the limit of detection sometimes can be improved by coupling a catalytic reaction to the reaction scheme. In electrochemical techniques, the lowest detection limits have been achieved when the catalytic reaction is coupled to systems that involve the adsorption of reagents [3–9]. The catalytic reaction works out as a homogeneous redox reaction that regenerates the initial redox form of the electroactive reagent, yielding an increase of its concentration close to the electrode surface and thus, of its respective signal of current.

Square-wave voltammetry (SWV) is one of the most used techniques for quantitative electroanalysis, since it provides fast and highly sensitive analyses due to its characteristics for applying potential and sampling current [10–14]. The net peak current (ΔI_p) is one of the most important parameters of SWV irrespectively it is used for analytical or for mechanistic purposes [10,15–20]. This is because the dependence of ΔI_p and its respective net peak potential (E_p) on experimental available parameters such as the SW frequency (f) and SW amplitude (E_{sw}) are important tools for maximizing the signal response as well as for characterizing the reaction mechanism of a given reaction [15,17,18,20–23]. There are different ways for making ΔI_p dimensionless and the selection of one of these ways usually depends on the presence of soluble or adsorbed species. In the case of reactions involving adsorbed species, the dependence of the dimensionless current ($\Delta \Psi_p$) on f commonly shows a maximum value for reactions with quasi-reversible charge transfer rate, which can be used for estimating the standard charge transfer rate constant (k_s) [11]. However, the use of the quasi-reversible maximum requires some particular attention, since its overuse can be tricky when the analyzed reaction scheme is not that simple [11,13,14,17,21–23].

Recently, we have reported a theoretical model for the Catalytic Adsorptive Stripping response of SWV [24]. The model considers a quasi-reversible electrode process coupled to a catalytic chemical

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reaction in which the reagent is adsorbed and the product is released to the solution. The adsorbed reactant is in equilibrium with its soluble part, which is a typical situation found in the adsorptive accumulation of traces of metal ions [3–5,7–9,21–23]. In that opportunity it was presented the mathematical solution of involved equations and a general description of different situations that can be found experimentally [24]. However, we did not know how to extract information of such a complex system without simulating and fitting the whole experimental voltammetric profiles. In this regard, it has to be considered that the possibility for using the quasi-reversible maximum to study the electrode kinetics depends on the values of k_{cat}, K_{ad}, f, E_{sw}, and of course k_s. As a result of this, it is not only difficult for experimentalists, but also for theoreticians to organize a strategy for detecting and understanding the effect of each variable separately.

This manuscript intends to provide a view of the whole system first, i.e. when all variables are affecting it at the same time, and then to suggest an organized study where the variables can be controlled one by one. Thus, if an experimental system matches to the present reaction scheme, where an electrochemical reaction is complicated by following homogeneous catalytic reaction, then it is advisable to consider the set of simple experimental steps included in the Conclusions section of this manuscript to estimate its kinetic and thermodynamic constants.

2. Mathematical model

The model has been developed for the analysis of the Catalytic Adsorptive Stripping response of a system studied by SWV at a bare electrode with flat surface [24]. The analysis of this system requires the following set of considerations:

First, it is assumed that the adsorption of the reactant follows a linear isotherm where the adsorption equilibrium has been achieved and where K_{ad} is the adsorption constant. This assumption requires low surface coverage of electroactive species, where there is no significant interaction between the adsorbed species. This is also suitable for the analysis of traces of a surface-active species.

Second, it is considered that the electrode reaction occurs through the adsorbed form of the oxidized species and releases the product in the solution, Eq. (1). Although it has been selected an oxidized species as reagent, this selection has been made for the sake of simplicity and the model can be used for studying both reductions or oxidation processes. The adsorption equilibrium of the reagent is reversible and so, the equilibrium between soluble and adsorbed species is rapidly achieved.

Third, the catalytic reaction is chemically irreversible. Thus, the general expression for the system can be generalized by the following set of reactions:

$$O_{(sol)} \overset{K_{ad}}{\rightleftharpoons} O_{(ads)} \underset{n}{\overset{k_s}{\rightleftharpoons}} R_{(sol)} \tag{1}$$

$$R_{(sol)} + Y_{(ex)} \overset{k'_{cat}}{\longrightarrow} O_{(sol)} \tag{2}$$

where Eq. (1) represents the adsorption equilibrium followed by the electrochemical step and Eq. (2) describes the catalytic reaction. The constant k_s is the standard heterogeneous surface rate constant and it is expressed in s^{-1}, while the adsorption constant K_{ad} is in cm. The constant k'_{cat} corresponds to a second order homogeneous rate constant of the catalytic reaction.

Fourth, it is assumed a large excess of the concentration of species Y, which is a typical condition for this kind of systems. Accordingly, the concentration of species Y remains constant and its bulk concentration (c_y^*) will determine the value of the pseudo-first order rate constant ($k_{cat} = c_y * k'_{cat}$). Therefore, Eq. (2) can be simplified as:

$$R_{(sol)} \overset{k_{cat}}{\longrightarrow} O_{(sol)} \tag{3}$$

Considering that the potential program of the stripping step corresponds to a cathodic SW scan that takes place in an unstirred solution, the time evolution of the species involved in Eqs. (1) and (3) can be described by the 2nd Fick's law as:

$$\partial c_r / \partial t = D(\partial^2 c_r / \partial x^2) - k_{cat} c_r \tag{4}$$

$$\partial c_o / \partial t = D(\partial^2 c_o / \partial x^2) + k_{cat} c_r \tag{5}$$

For the resolution of Eqs. (4) and (5), it is assumed that all involved species have a common diffusion coefficient value, $D = 4 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$. However, the solution of these equations is not restricted to this single value of D. In this regard, the typical values of D associated with analytes in aqueous or organic solutions do not significantly affect the shape of calculated SW voltammograms. Besides, it is considered that the reaction scheme of Eqs. (1) and (3) can be described by the following boundary conditions:

$$t = 0, x \geq 0: c_r + c_o = c_o^* \tag{6}$$

$$\Gamma_o^{ini} = K_{ad} c_o^* \tag{7}$$

$$c_r = c_r^* = 0 \tag{8}$$

$$t > 0, \quad x \to \infty: \quad c_o \to c_o^* \tag{9}$$

$$c_r \to 0 \tag{10}$$

$$x = 0: D(\partial c_o / \partial x)_{x=0} = I/nFA - \partial \Gamma_o / \partial t \tag{11}$$

$$D(\partial c_r / \partial x)_{x=0} = -I/nFA \tag{12}$$

$$I(t)/nFA = k_s \exp[-\alpha \, \varphi(t)] \{ (\Gamma_o)_{x=0} - (c_r)_{x=0} \, r_s \exp[\varphi(t)] \} \tag{13}$$

$$\Gamma_o = K_{ad} (c_o)_{x=0} \tag{14}$$

$$\varphi(t) = nF[E(t) - E_{ad}^{o'}]/RT \tag{15}$$

where $E(t)$ is the square-wave potential function, n is the number of exchanged electrons, and A is the electrode surface area. The auxiliary constant $r_s = 1$ cm is commonly introduced in the Butler-Volmer expression, Eq. (13), to unify the dimensions of $O_{(ad)}$ and $R_{(sol)}$ species [11–15]. However, the constant r_s is expressed in centimeters and so, it requires a physical meaning. According to the Born–Oppenheimer approximation, once $O_{(ad)}$ is transformed into $R_{(sol)}$ the latter "appears" exactly at the same place than the species $O_{(ad)}$ used to be. Thus, although $R_{(sol)}$ does not interact physically neither chemically with the surface, it appears at the surface and then diffuses to the bulk. Since there is no kind of partition of $R_{(sol)}$ with the surface, the value of r_s is always equal to 1 cm. $E_{ad}^{o'}$ has been set as 0 V and it is related to $E^{o'}$, which is the formal potential for a simple redox reaction by [15,16]:

$$E_{ad}^{o'} = E^{o'} + (RT/nF) \ln(K_{ad}/r_s) \tag{16}$$

The cathodic current has been defined as positive, Eqs. (11)–(13). Other symbols have their usual meaning. The current is normalized according to:

$$\Psi(t) = I(t) [nFAc_o^* K_{ad} f]^{-1} \tag{17}$$

where f is the square-wave frequency. To resolve the differential Eqs. (4) and (5) it is necessary to introduce the following change of variables [25]:

$$\phi = c_r + c_o \tag{18}$$

$$\theta = c_r \exp(k_{cat} t) \tag{19}$$

Thus, a new set of equations is obtained in terms of variables ϕ and θ [25]:

$$\partial \phi / \partial t = D(\partial^2 \phi / \partial x^2) \tag{20}$$

$$\partial\theta/\partial t = D(\partial^2\theta/\partial x^2) \tag{21}$$

$$D(\partial\phi/\partial x)_{x=0} = -\partial\Gamma_0/\partial t \tag{22}$$

$$D(\partial\theta/\partial x)_{x=0} = -I\,\exp(k_{cat}t)/nFA \tag{23}$$

These equations are then transformed into the Laplace domain where the respective set of boundary conditions is considered. After this step, the variables are changed back to c_r and c_o. Then, the resulting equations are changed to the time domain where the following functions for the time evolution of c_o and c_r at the electrode surface are obtained:

$$c_{o,x=0} = c_o^* - \int_0^t \frac{I(\tau)\exp[-k_{cat}(t-\tau)]a\exp[a^2(t-\tau)]\operatorname{erfc}[a\sqrt{(t-\tau)}]d\tau}{nFA\sqrt{D}} \tag{24}$$

$$c_{r,x=0} = \int_0^t \frac{I(\tau)\exp[-k_{cat}(t-\tau)]d\tau}{nFA\sqrt{D\pi(t-\tau)}} \tag{25}$$

The expression for the current is obtained by using the numerical integration method suggested by Nicholson and Olmstead [26]:

$$\Psi_{(m)} = \{1 - \xi\Xi_{a(m)} - [\varsigma + T_{(m)}]\Xi_{b(m)}\}\{\aleph_{(m)} + \xi\Xi_{a(1)} + [\varsigma + T_{(m)}]\Xi_{b(1)}\}^{-1} \tag{26}$$

where $a = D^{1/2}(K_{ad})^{-1}$; $b = (a^2 - k_{cat})$; $\xi = f\ b^{-1}$; $\varsigma = a\xi k_{cat}^{-1/2}$; $T_{(m)} = r_s\ f\ (D\ k_{cat})^{-1/2}\exp[\varphi_{(m)}]$; $\Xi_{a(m)} = \sum_{j=1}^{m-1}\Psi_{(j)}\ Q_{(i)}$; $\Xi_{b(m)} = \sum_{j=1}^{m-1}\Psi_{(j)}\ S_{(i)}$; $\aleph_{(m)} = f\ k_s^{-1}\ \exp[\alpha\varphi_{(m)}]$; $S_{(i)} = \operatorname{erf}[(k_{cat}\ \delta\ i)^{1/2}] - \operatorname{erf}[(k_{cat}\ \delta(i-1))^{1/2}]$; $Q_{(i)} = \exp[(b\ \delta\ i]\operatorname{erfc}[a\ (\delta\ i)^{1/2}] - \exp[b\ \delta\ (i-1)]\operatorname{erfc}[(a\ \delta(i-1))^{1/2}]$; $i = m - j + 1$; $\delta = (q\ f)^{-1}$. The dimensionless expression $a(\delta)^{1/2}$ represents the influence of the mass transfer with regards to the adsorption of electroactive species and the time scale of the experiment, while the expression $b(\delta)$ considers also the effect of the catalytic reaction. Typical values of D do not affect the shape of calculated SW voltammograms. The value of q corresponds to the number of sub-intervals used for the numerical integration steps. A value of $q = 50$ provides a numerical error lower than 0.5% and the voltammograms can be calculated in few seconds [24]. The authors are positive to assist to those researchers interested on learning more about the mathematics and software described in this manuscript.

3. Results and discussion

3.1. Don't forget the forward and backward currents

Usually, experimentalists and theoreticians focus their analyses on the behavior of the dimensionless net current ($\Delta\Psi = \Psi_f - \Psi_b$) with regards to experimentally available parameters such as f and E_{sw}. However, there is still some relevant information in the voltammetric profiles of the forward (Ψ_f) and backward (Ψ_b) currents that should not be discarded. Although the scheme of Eqs. (1) and (3) considers the reduction of an adsorbed species, the opposite redox process can be deduced without significant complications.

Fig. 1 shows theoretical voltammograms calculated for reactions with electrochemical charge transfer processes corresponding to reversible, quasi-reversible, and irreversible kinetics. Curves 1A are related to systems with low catalytic rate constant, while the sigmoid shape of curves 1F evidences the prevalence of the catalytic process in the whole electrochemical reaction. Curves calculated with $k_{cat} < 0.1\,\mathrm{s}^{-1}$ have basically the same shape than curves 1A. Thus, the effect of a catalytic reaction with $k_{cat} < 0.1\,\mathrm{s}^{-1}$ would be negligible from the experimental point of view and it could only be detected from theoretical results. The existence of a coupled catalytic process produces an increment on the absolutes value of Ψ_f and Ψ_b measured around 0.2 V after the voltammetric peak, see the arrows. Although this variation in the current at the limiting cathodic region is negligible for

the case of $k_{cat} = 0.1\,\mathrm{s}^{-1}$, it becomes quite significant for $k_{cat} > 10\,\mathrm{s}^{-1}$. When systems involving adsorbed species are studied by SWV, the current sampled at the limiting cathodic region is typically zero [11–16]. This is because the adsorbed reactant is completely consumed at the time in which the current is sampled, while the product does not significantly react at those potentials. For the reaction scheme described by Eqs. (1) and (3), the surface concentration and the concentration gradient of the oxidized species are affected by the catalytic process. Since the current at the limiting cathodic region is commonly controlled by the diffusion of involved reagents, that current has been denominated limiting current of the system (Ψ_{lim}). In this kind of reactions, however, it is important to notice that the value of Ψ_{lim} depends more on k_{cat} than on D. The behavior of Ψ_{lim} can be studied from a plot of Ψ_f and Ψ_b components, but not from the voltammetric response of $\Delta\Psi$. In this regard, voltammograms of $\Delta\Psi$ corresponding to the different situations presented in Fig. 1 consist on bell-shaped curves that hide most of the mechanistic information associated with the system, not shown.

SW voltammograms calculated for $k_{cat} > 300\,\mathrm{s}^{-1}$ exhibit sigmoid shapes similar to those of curves 1F. Under these conditions, the onset potential is controlled by k_s and the value of Ψ_{lim} changes proportionally to the value of k_{cat} (see the arrows included for the irreversible case). The curves 1A show that the limiting current observed at very negative potentials is null when the catalysis is negligible. This is the typical behavior of reactions involving adsorbed species [11,13,14]. Since the current is conditioned by the amount of adsorbed species, it becomes null when the adsorbed species are totally consumed. Under these conditions, the contribution of the diffusive term would be evident only when the adsorption constant is very low, not shown. However, when the catalytic reaction releases oxidized species at the close proximity of the electrode surface, the value of the limiting current will increase as a function of k_{cat}, see from curves 1B to curves 1F.

Although the effect of k_{cat} is more easily observed for irreversible reactions, the analysis of the limiting current shows that this value is independent of the electrochemical charge transfer kinetic. From the analysis of Ψ_{lim} versus the effects of k_{cat} and f, it is found that the dimensionless limiting current depends linearly on both parameters. The equation obtained from a set of linear regressions is:

$$|\Psi_{lim}| = k_{cat} \times f^{-1} \tag{27}$$

This result differs from that obtained for cyclic voltammetric curves of a system without adsorbed species where the authors found that Ψ_{lim} depends on the square root of k_{cat} [27,28].

3.2. The quasi-reversible maximum vs frequency

The values of current observed in Fig. 1A and B show that the largest currents correspond to quasi-reversible reactions while the lowest values belong to irreversible charge transfer processes. As a result, the net peak current ($\Delta\Psi_p$) will show maximum values, when it is plotted as function of f, for reactions with charge transfer in the quasi-reversible range. This last outcome is well-known for electrochemical reactions involving adsorbed reagents where $\Delta\Psi_p$ develops the so-called quasi-reversible maximum [15,16]. Although, this maximum can be used for estimating the value of k_s, it cannot be observed for every reaction with adsorbed species, Fig. 1D and F. In this regard, it is important to assign a reaction mechanism for the experimental system, then compare experimental with theoretical curves, and finally estimate the charge transfer rate constant from the position of the quasi-reversible maximum.

Fig. 2 shows the dependence of $\Delta\Psi_p$ on f. Curves 2(a) have been calculated for systems with irreversible charge transfer, while curves 2(e) correspond to reversible electrochemical processes. Although, it is expected that under these two situations the dimensionless net currents remain constant with the time scale, this asseveration is right only for the case of very slow catalytic reactions, Fig. 2A. However, the value of
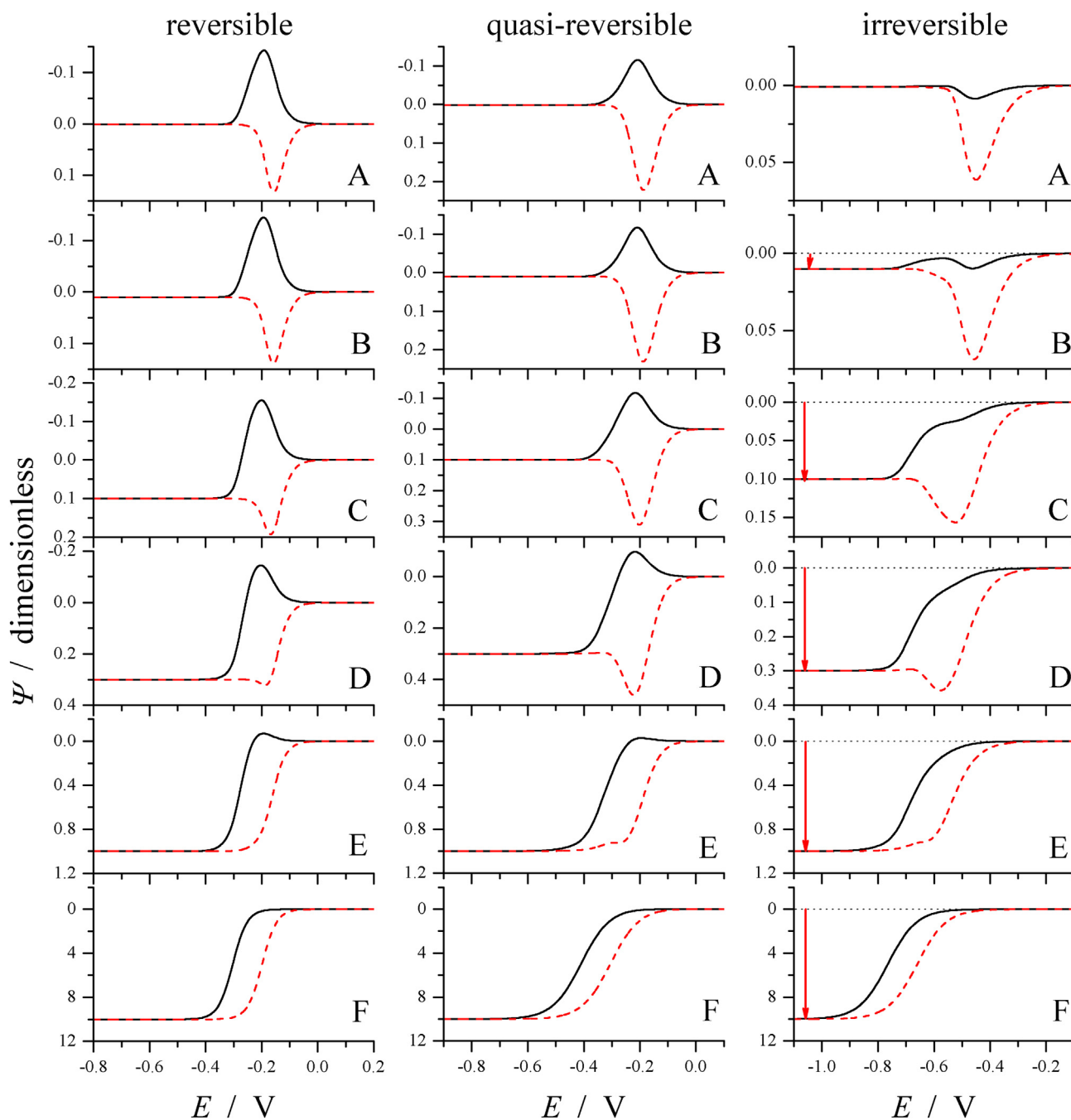
Fig. 1. Theoretical Ψ–E profiles calculated with Eq. (26) for $f = 100$ Hz, $E_{sw} = 50$ mV, $dE = 5$ mV, $n = 1$, $\alpha = 0.5$, $K_{ad} = 0.3$ cm, $k_s/\text{s}^{-1} = 10^3$ (reversible), 1 (quasi-reversible) and 10^{-3} (irreversible), and $k_{cat}/\text{s}^{-1} = 0.1$ (A), 1 (B), 10 (C), 30 (D), 100 (E), and 1000 (F).

$\Delta\Psi_p$ might show significant variation depending on the catalytic contribution. The presence of the catalytic reaction increases the value of $\Delta\Psi_p$ calculated for the lowest values of f, Fig. 2A and B. The value of f corresponding to the quasi-reversible maximum (f_{max}) can be studied for reactions without or with minimum contribution of the catalytic step. More specifically, the value of f_{max} is not affected by k_{cat} for systems with $k_{cat} < 1\text{ s}^{-1}$. Above this value of k_{cat}, however, the catalytic contribution would hinder finding a maximum from the dependence of $\Delta\Psi_p$ on f, see curves 2(b–d). Thus, provided $k_{cat} < 1\text{ s}^{-1}$, it is feasible to use Eq. (28) for estimating k_s from the value of f_{max}. To do this, experimentalists should diminish the contribution of the catalytic reaction until observe that the value of Ψ_{lim} has become around 5% of Ψ_f, see Fig. 1B. The contribution of the catalytic reaction could be minimized by decreasing the concentration of the catalyst or eventually by varying the solution pH.

$$f_{max} = -1.16 + 51\, k_s^{1.25} \qquad (28)$$

The variation of f does not only affect the apparent kinetics of the charge transfer reaction, but also that of the catalytic process. To understand the effect of f on the kinetics of this electrochemical system it is necessary to evaluate the behavior of $\Delta\Psi_p$ as a function of the logarithms of k_s and k_{cat}, Fig. 3. Two different analyses are presented in this figure. The mesh shows the dependence of $\Delta\Psi_p$ on the values of $\log(k_s f^{-1})$ and $\log(k_{cat} f^{-1})$ for SW voltammograms calculated for $f = 100$ Hz and where the values of k_s and k_{cat} have been varied, while the curves show the behavior of $\Delta\Psi_p$ for a set of selected values of k_s and k_{cat} where f is changed from 2 to 2000 Hz. Accordingly, the data used for the mesh correspond to a set of different electrode reactions (e.g., the analysis of
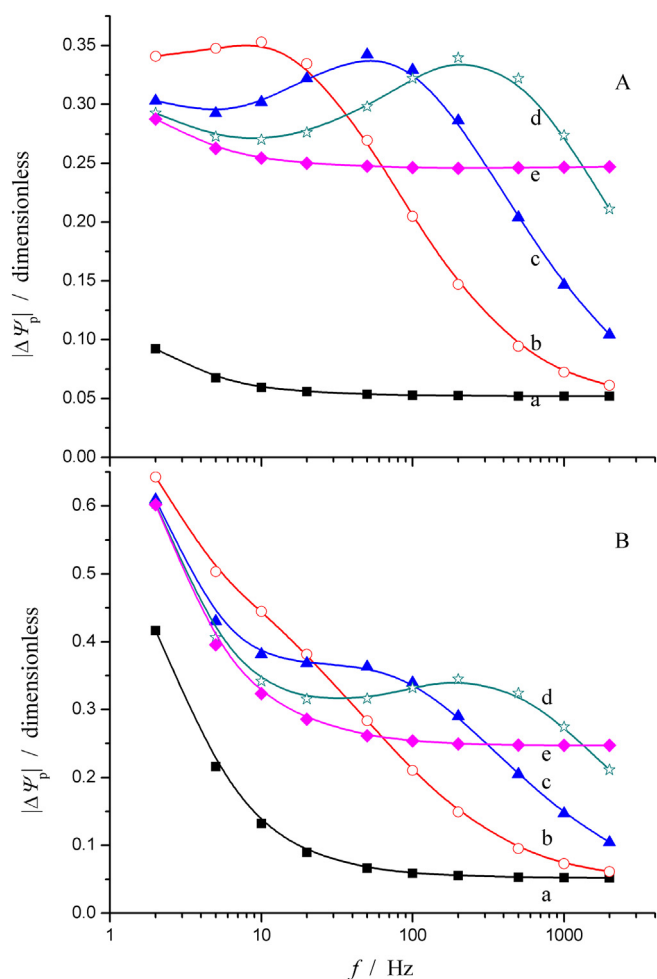
Fig. 2. Dependence of $\Delta\Psi_p$ on f for systems with $k_{cat}/s^{-1} = 0.1$ (A), 1 (B). The curves were calculated with Eq. (26) for $E_{sw} = 50$ mV, $dE = 5$ mV, $n = 1$, $\alpha = 0.5$, $K_{ad} = 0.3$ cm, and $k_s/s^{-1} = 0.001$ (a), 0.3 (b), 1 (c), 3 (d), and 1000 (e).

systems with different k_s and k_{cat} values), while each curve of this figure shows the behavior of a single electrode reaction (e.g., the variation of f for a system with constant values of k_s and k_{cat}).

Provided the influence of the catalytic contribution is relatively low, $\log(k_{cat}\,f^{-1}) < -1$, the surface plot would indicate that the value of $\Delta\Psi_p$ does not depend on f for reversible reactions, $\log(k_s\,f^{-1}) > -1$, neither for irreversible reactions, $\log(k_s\,f^{-1}) < -4$. Besides, it could be considered that quasi-reversible reactions would exhibit a maximum when $\log(k_{cat}\,f^{-1}) < 0$. Above this value, the effect of the catalytic component would control the shape of voltammetric curves and so, the dependence of $\Delta\Psi_p$ on f. Unfortunately, from the experimental point of view, it is not possible to estimate k_s from the analysis of f_{max} if $k_{cat} \geq 10\,s^{-1}$. This is because the variation of f changes the apparent kinetics of both, the catalytic and the voltammetric contributions. Thus, the region where the quasi-reversible maximum develops is rather limited, since the dependence of $\Delta\Psi_p$ on f moves though a diagonal that crosses the surface defined by $\log(k_s\,f^{-1})$ and $\log(k_{cat}\,f^{-1})$. Curves 3(b–d) correspond to a set of systems with kinetic constants that should present the quasi-reversible maximum. However, the quasi-reversible maximum can be roughly noticed in curve 3b.

When a chemical reaction is coupled to an electrochemical system that involves adsorbed species, not only the dependence of $\Delta\Psi_p$ on f becomes more complicated than usual, but also the one of E_p. The surface of Fig. 4 shows the dependence of E_p on the values of $\log(k_s\,f^{-1})$ and $\log(k_{cat}\,f^{-1})$ for SW voltammograms calculated with $f = 100$ Hz.
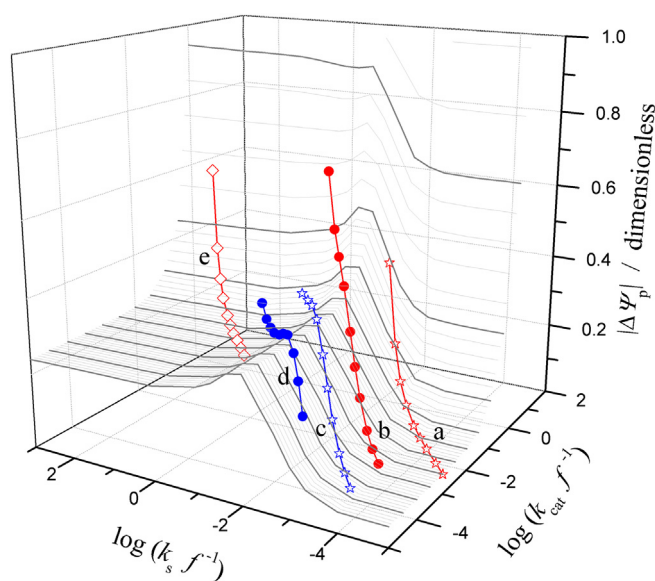
Fig. 3. Dependence of $\Delta\Psi_p$ on $\log(k_s\,f^{-1})$ and $\log(k_{cat}\,f^{-1})$ for $\alpha = 0.5$, $n = 1$, $dE = 5$ mV, $E_{sw} = 50$ mV, $f = 100$ Hz, $K_{ad} = 0.3$. Curves (a–e), dependence of $\Delta\Psi_p$ on $\log(k_s\,f^{-1})$ and $\log(k_{cat}\,f^{-1})$ when the value of f is varied from 2 to 2000, for $k_{cat} = 1\,s^{-1}$ and $k_s = 0.01\,s^{-1}$ (a), for $k_{cat} = 1\,s^{-1}$ and $k_s = 0.3\,s^{-1}$ (b), for $k_{cat} = 0.1\,s^{-1}$ and $k_s = 0.3\,s^{-1}$ (c), for $k_{cat} = 0.1\,s^{-1}$ and $k_s = 3\,s^{-1}$ (d), and for $k_{cat} = 1\,s^{-1}$ and $k_s = 300\,s^{-1}$ (e). Other parameters are the same of the surface.
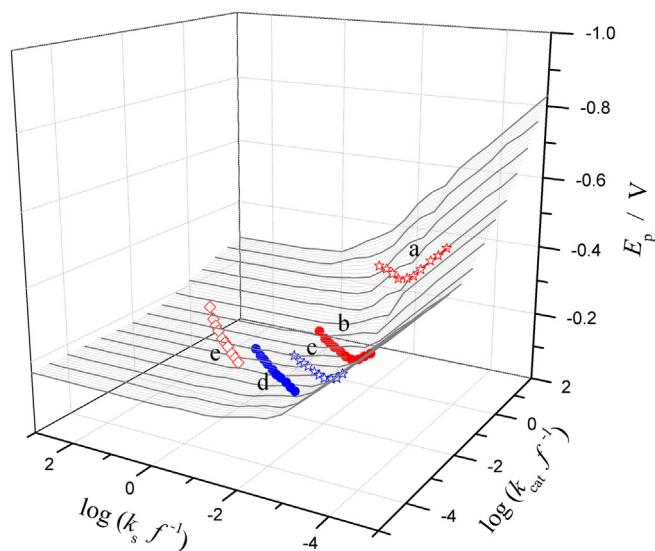
Fig. 4. Dependence of SW E_p on $\log(k_s\,f^{-1})$ and $\log(k_{cat}\,f^{-1})$ for $\alpha = 0.5$, $n = 1$, $dE = 5$ mV, $E_{sw} = 50$ mV, $f = 100$ Hz, $K_{ad} = 0.3$. Curves (a–e), dependence of E_p on $\log(k_s\,f^{-1})$ and $\log(k_{cat}\,f^{-1})$ when the value of f is varied from 2 to 2000, for $k_{cat} = 1\,s^{-1}$ and $k_s = 0.01\,s^{-1}$ (a), for $k_{cat} = 1\,s^{-1}$ and $k_s = 0.3\,s^{-1}$ (b), for $k_{cat} = 0.1\,s^{-1}$ and $k_s = 0.3\,s^{-1}$ (c), for $k_{cat} = 0.1\,s^{-1}$ and $k_s = 3\,s^{-1}$ (d), and for $k_{cat} = 1\,s^{-1}$ and $k_s = 300\,s^{-1}$ (e). Other parameters are the same of the surface.

The curves of Fig. 4 show the behavior of E_p for a set of voltammetric profiles calculated for $2 < f/\text{Hz} < 2000$. It should be noticed that the plot of Fig. 4 is rotated with regards to that of Fig. 3. Again, the data used for the mesh correspond to a set of different electrode reactions (e.g., the analysis of systems with different k_s and k_{cat} values), while each curve of this figure shows the behavior of a single electrode reaction (e.g., the variation of f for a system with constant values of k_s and k_{cat}). The flat region placed at the bottom of this 3D-plot corresponds to systems with reversible charge transfer reactions and low catalytic rate
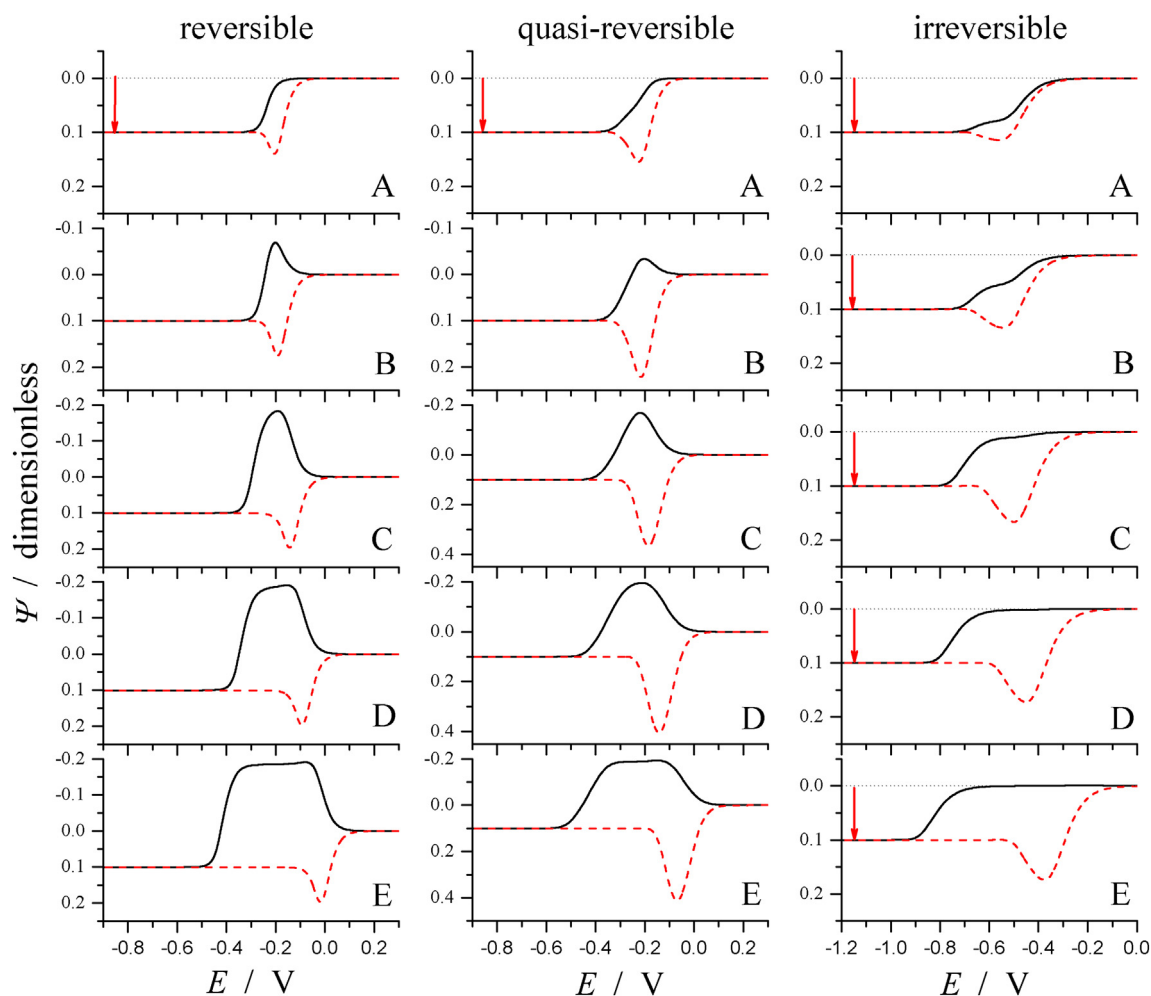
Fig. 5. Theoretical Ψ–E profiles calculated with Eq. (26) for f = 100 Hz, dE = 5 mV, n = 1, α = 0.5, K_{ad} = 0.3 cm, k_s/s^{-1} = 10^3 (reversible), 1 (quasi-reversible) and 10^{-3} (irreversible), k_{cat} = 10 s^{-1}, and E_{sw}/mV = 10 (A), 25 (B), 75 (C), 125 (D), and 200 (E).

constant. Under this condition, the value of E_p will be constant for systems with reversible charge transfer and with $k_{cat} < 0.1\,s^{-1}$. At the backside of Fig. 4, there is a region corresponding to reversible electrochemical reactions with significant catalytic contribution. The values of E_p of these systems change (-35 ± 5) mV per decade if $k_{cat} > 10\,s^{-1}$. Finally, at the front side of Fig. 4, there is a region where the value of E_p changes (105 ± 5) mV per decade. This last region corresponds to irreversible electrochemical reactions with low catalytic contribution, i.e. $k_{cat} < 0.1\,s^{-1}$.

It is difficult to establish other linear dependences of E_p on f when $k_{cat} > 0.1\,s^{-1}$. As it can be observed from curves 4(a–e), the behavior of E_p as a function of f can be very different. These variations can be linear or not, depending on the values of k_{cat} and k_s. The catalytic contribution diminishes with the increment of f while the apparent reversibility of the charge transfer reaction does the opposite. As a result, the value of E_p can decrease for a given time scale and then increase, curves 4(a–c).

3.3. The quasi-reversible maximum vs the adsorption constant

The variation of K_{ad} from 0.1 cm to 100 cm does not change the values of $\Delta\Psi_p$, neither the value of f_{max}, [11]. With regards to the dependence of E_p on K_{ad}, this behavior is given by Eq. (16) [15,16]. Nevertheless, it has to be considered that the adsorption constant corresponds to a linear isotherm where any kind of interaction between adsorbed species has been neglected. These conditions are commonly suitable for simulating systems corresponding to the trace analysis of

metal complexes.

3.4. The effect of SW amplitude

Fig. 5 shows SW voltammograms calculated for reversible, quasi-reversible, and irreversible reactions where the value of E_{sw} has been ranged from 10 mV to 200 mV. All profiles were simulated with a value of $k_{cat} = 10\,s^{-1}$. As a result of this, the same value of Ψ_{lim} has been found for all simulated voltammograms. Although this should be the expected result, after the analysis of Fig. 1 and Eq. (27), it is still an interesting outcome because it confirms that the value of Ψ_{lim} does not depend on E_{sw}, see the arrows. As it was discussed above, the variation of f affects the apparent kinetics of the chemical and the electrochemical steps. Although the variation of E_{sw} also changes the kinetics and modifies the size and shape of voltammetric responses, it does not affect the dimensionless kinetic parameters $(k_s f^{-1})$ and $(k_{cat} f^{-1})$ of the system. Curves 5A have been plotted using the same scale and calculated for E_{sw} = 10 mV, which is a rather small value of SW amplitude. As a consequence of this, Ψ_f does not show a peak, while Ψ_b exhibits peaks of different size. The adsorption process is responsible of the shape of the peaks observed for Ψ_b. When adsorbed species are involved, SW voltammograms can exhibit peaks with shapes that are similar to that of a Gaussian curve [11,14–16]. In this case, however, the bell-shaped curve is observed for Ψ_b, which depends on the concentration gradient of $R_{(sol)}$. In this regard, it is worth to remember that Eq. (8) indicates that all reduced product is coming from the electrochemical reduction of $O_{(ads)}$. Thus, even though Ψ_b corresponds to the
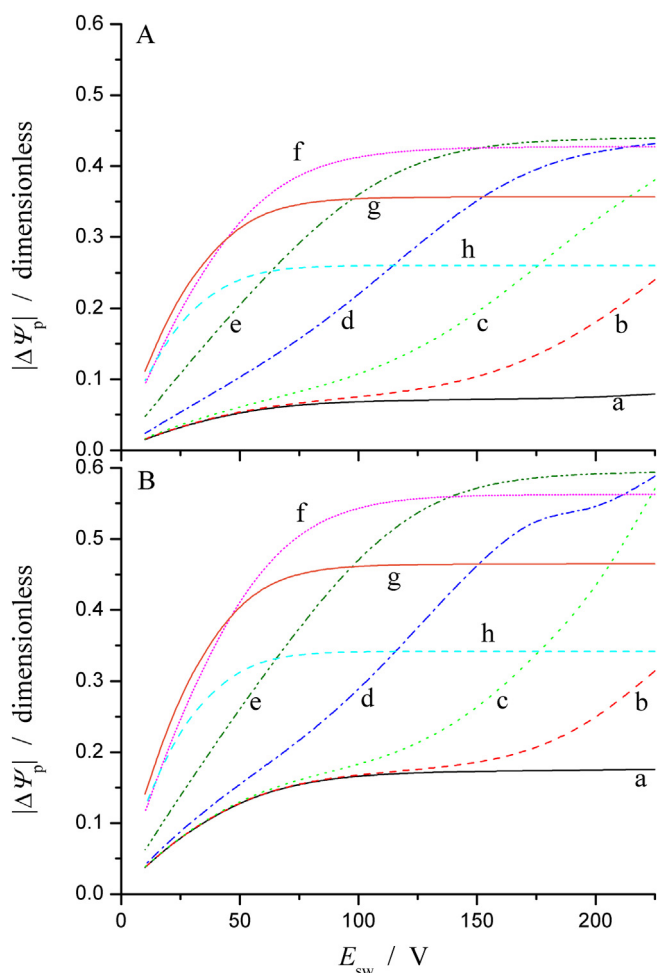
Fig. 6. Dependence of $\Delta\Psi_p$ on E_{sw} obtained from voltammetric curves calculated with Eq. (26) for $f = 100$ Hz, $dE = 5$ mV, $n = 1$, $K_{ad} = 0.3$ cm, $\alpha = 0.5$, (A) $k_{cat} = 0.3$ s^{-1} and (B) $k_{cat} = 10$ s^{-1}. k_s/s^{-1} = (a) 0.001, (b) 0.01, (c) 0.03, (d) 0.1, (e) 0.3, (f) 1, (g) 3, and (h) 1000.

species $R_{(sol)}$, its concentration profile is conditioned by the adsorption process of the oxidized reagent. This outcome depends on the existence of an adsorbed reagent that releases one or more soluble products [13]. Since the presence of a catalytic reaction produces an increment on the limiting current, the shape of Ψ_b can be considered as the addition of a sigmoid curve and a bell-shaped curve corresponding to the catalytic and the adsorption processes, respectively. Reversible and irreversible charge transfer reactions present rather small bell-shaped curves when they are compared to a quasi-reversible process. This is because the charge transfer reaction is either too fast or too slow with regards to the time scale of the measurement. In the case of reversible electrochemical reactions, most of the electroactive species has been consumed when the current is sampled, while irreversible reactions are inherently very slow. The largest peaks of Ψ_b correspond to quasi-reversible electrochemical reactions because they have the most suitable relationship between the rate of consuming adsorbed species and the time-scale of the experiment.

Fig. 6 shows the dependence of $\Delta\Psi_p$ on E_{sw} for a set of reactions with different k_s values where two values of k_{cat} have been considered. The curves included in Fig. 6A correspond to systems where the contribution of the catalytic reaction is practically negligible, while the profiles analyzed in Fig. 6B have significant contribution of the catalytic reaction. From the comparison of Fig. 6A and B it is possible to conclude that the dependences of $\Delta\Psi_p$ on E_{sw} are similar, for a given value of k_s, but the magnitudes increase according to the value of k_{cat}. It was not

possible to find a simple equation that describes the dependence of $\Delta\Psi_p$ on E_{sw} for an unknown set of k_{cat} and k_s values. However, the amount in which the curves of Fig. 6B have been increased with regards to those of Fig. 6A is practically the same than the value of Ψ_{lim}. In consequence, it should be possible to estimate the value of k_s by comparing experimental data with the curves included in Fig. 6. One of the reasons for this comparison is that the variation of E_{sw} does not change the apparent reversibility of the chemical neither the electrochemical contributions. Another reason consists on that sometimes the presence of Y species, which is commonly the analyte, cannot be decreased to zero in real experiments. Under these conditions, it is difficult to observe the quasi-reversible maximum if $k_{cat} > 1$ s^{-1}, and so, to estimate the value of k_s.

It is important to consider that, a quick inspection of the curves included in Figs. 1 and 5 should be enough to determine if the experimental system corresponds to a reversible, quasi-reversible, or irreversible situation and even to estimate the value of the catalytic contribution. This is because the value of k_{cat} can be calculated from Eq. (27). Then, if it were possible to decrease the catalytic contribution to a negligible value, the experimentalist should be able to determine k_s by analyzing the quasi-reversible maximum. However, if the value of k_{cat} could not be diminished, the value of the charge transfer rate constant should be estimated from the curves of Fig. 6A and B. Experimentalists should measure the dependence of $\Delta\Psi_p$ on E_{sw} and subsequently they have to subtract the value of Ψ_{lim} from the obtained data. The resulting curve should be then compared with the curves of Fig. 6A to estimate the value of k_s. It is not necessary to perform measurements of SWV up to $E_{sw} = 225$ mV, since most experimental systems do not allow it. In fact, the value of k_s can be estimated also from data corresponding to a smaller range of E_{sw}, i.e. $10 < E_{sw}/\text{mV} < 100$.

4. Conclusion

The theoretical response of SWV for the general case of systems involving adsorbed species with quasi-reversible electron-transfer complicated by a coupled following quasi-reversible homogeneous catalytic reaction has been presented. The variation of frequency affects the apparent kinetics of the catalytic and the electrochemical contributions. The first advice we can provide for the analysis of complicated systems like this is to compare experimental profiles with theoretical curves in order to ensure that the model is good enough to extract some kinetic information from the experimental system. From the normalization of current, suggested in Eq. (17), it should be quite simple to estimate K_{ad} from the ratio between $\Delta\Psi_p$ and ΔI_p. This is because is all variables in Eq. (17), except the value of K_{ad}, are usually known. However, the estimation of K_{ad} cannot be made for systems with $k_{cat} > 100$ s^{-1}, because the catalytic contribution would determine the size and shape of the current signal, see Fig. 1, curves F. Second, it is important to consider the value of Ψ_{lim} can be observed from a plot of Ψ_f and Ψ_b, but not from one of $\Delta\Psi$. The value of Ψ_{lim} depends on k_{cat}, and it can be used for estimating k_{cat} by employing Eq. (27). After doing this, the experimentalist should decrease the contribution of the catalytic process in the voltammetric curve. This could be achieved rather easily in the case of pseudo-first order reactions, since it would be only necessary to decrease the concentration of Y species given that $k_{cat} = c_y * k'_{cat}$. Under such condition, the quasi-reversible maximum should be well-defined and the value of k_s can be estimated by using Eq. (28). However, there are experimental systems where the catalytic step cannot be made negligible [29]. If that were the case, the experimentalist has to remember that the quasi-reversible maximum might not be observed because it is conditioned by the values of k_{cat} and k_s. Accordingly, once the analysis of Ψ_{lim} has been made, it is possible to estimate the value of k_s from a plot of $\Delta\Psi_p$ as a function of E_{sw}. Although not all experimental systems can be evaluated using very high of E_{sw} values, the slopes and trends observed for $E_{sw} < 100$ mV should be a notable contribution for estimating the value of k_s.

Acknowledgements

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