

Study of the Electrocatalytic Reaction of Hydrogen Peroxide Mediated by Azobenzene Monolayer with Several Multipotential Pulse Techniques

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Abstract: The comparison between the response corresponding to a simple charge transfer taking place at an electroactive monolayer with that of an electrocatalytic process at a modified electrode are presented by using the multipulse potential techniques cyclic staircase voltammetry (CSCV) and cyclic square wave voltammetry (CSWV). General analytical and explicit equations for the $I-E$ responses have been tested by means of the study of the reduction of azobenzene monolayer at mercury electrode. The value of the chemical rate constant ($k_c = 40 \text{ M}^{-1}\text{s}^{-1}$) has been easily obtained from the cathodic plateau of the CSCV curves and from the best fitting between theoretical and experimental CSWV curves.

Keywords: Azobenzene, hydrogen peroxide, catalytic mechanism, monolayer, multipotential pulse techniques.

1. INTRODUCTION

The development of monolayer-functionalized surfaces has been a successful trend in the characterization and control of electrochemical reaction kinetics and catalysis [1-4]. The modification of the electrode surface can be carried out by different routes, the covalent attachment of redox species being one of the most used [1, 2, 5-7].

Azobenzene-terminated self-assemble monolayers are extensively used in studies of electron-transfer processes [8]. The chemical composition, structure and length of the molecules linked to the surface *via* mercury electrode as well as the dielectric environment on the surface are all crucial factors determining the dynamics of the electron transfer between the azobenzene and the electrode surface [9].

Among the broad variety of electrochemical techniques, cyclic multipotential pulse techniques, such as CSCV and CSWV, are powerful tools for the characterization of the response of species immobilized on the electrode surface [2, 10-15]. Those techniques are based on the application of a sequence of potential pulses of discrete nature and, especially, CSWV, present several advantages, one of the most important being their widely acknowledged inherent ability to decouple faradic currents from non faradaic ones [15-17].

Analytical and easy manageable expressions for the current of a simple charge transfer process and of an electrocatalytic process at mediator modified electrodes for any multipotential pulse technique were deduced in previous papers [13, 14, 18, 19].

In order to check the validity of the above mentioned expressions and characterize the azobenzene/ hydrogen peroxide system, we have analysed and compared the response corresponding to the reduction of the azobenzene at

a mercury electroactive monolayer with that of the redox reaction of azobenzene in the presence of hydrogen peroxide as oxidizing agent. From our results, we have observed that azobenzene presents strong adsorption, behaves as quasi-reversible at a mercury electrode and is also influenced by pH conditions.

2. EXPERIMENTAL SECTION

2.1 Materials and Procedures

Ethanol, KNO_3 , H_2O_2 (Merck, reagent grade), and sodium citrate tribasic dehydrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$), citric acid ($\text{C}_6\text{H}_8\text{O}_7$) and azobenzene (AZB) (Aldrich, reagent grade) were used as received. AZB was dissolved in ethanol, and then diluted with water until the final proportion of ethanol was 1%. AZB was adsorbed at the mercury surface at a rest potential $E_{\text{rest}} = -0.200 \text{ V}$ versus reference for 10 s prior to measurements such that all the measurements were taken when the surface coverage of this species had reached equilibrium with the bulk concentration.

The low azobenzene concentration used ($30 \mu\text{M}$) guarantees that any possible contribution to the whole response due to dissolved azobenzene can be considered as negligible. Moreover, we have checked that desorption has not taken place in the time scale of the experiments (see also [20, 21]).

2.2. Aparatus

CSCV and CSWV were performed by using a computer-driven potentiostat-galvanostat designed and constructed by Quiceltron.

A three-electrode cell was employed in the experiments. A homemade static mercury drop electrode (SMDE) served as working electrode. The electrode radius of the SMDE was determined by weighing a large number of drops. The counter electrode was a Pt foil and the reference electrode was a Ag/AgCl , KCl (saturated) electrode. Solutions were prepared with distilled deionized water (Milli-Q filtering system). Nitrogen gas was passed through solutions for de-aeration for 20 min prior to measurements, with nitrogen

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atmosphere maintained over the solution during all the experiments. All the kinetic and thermodynamic values obtained for the AZB system correspond to series of five essays. The results are the mean of the five experimental values. The errors correspond to the standard deviation.

To avoid transport effects in the catalytic response, a magnetic stirrer with a constant rotation rate was placed close to the electrode surface, so a constant agitation was maintained during the whole experiment. By proceeding in this way we have checked that the values of the catalytic pseudo first order rate constant obtained do not depend on the H₂O₂ concentration.

3. RESULTS AND DISCUSSION

3.1 E mechanism at a Modified Electrode

In previous papers we have deduced an analytical and easy manageable expression for the current corresponding to a simple charge transfer process of any reversibility degree and any sequence of consecutive potential steps designed by $E_1, E_2, \dots, E_{p-1}, E_p$, of the same length τ . This expression is applied to the following process, $A + ne^- \xrightleftharpoons[k_{ox}]{k_{red}} B$, where the redox couple A/B is immobilized at the electrode surface [13, 14, 22, 23] and k_{red} and k_{ox} are the electrochemical rate constants of the forward (reduction) and backward (oxidation) heterogeneous processes, respectively [14, 15]:

$$\frac{I_p}{Q_{MAX}} = k_{red,p} - k_{E,p} \sum_{j=1}^{p-1} \left(\frac{k_{red,j}}{k_{E,j}} (1 - \theta_j) \prod_{l=j+1}^{p-1} \theta_l \right) \theta_p \quad (1)$$

with

$$\theta_p = \exp(-k_{E,p} \tau) \quad (2)$$

$$k_{E,p} = k_{red,p} + k_{ox,p} \quad (3)$$

$Q_{MAX} = nFS\Gamma_T$, where S is the electrode area, n the number of transferred electrons and Γ_T the total electroactive surface excess.

Eq. (1) is applicable for different multipotential step techniques. In this paper we will apply this equation to CSCV and CSWV which are among those most frequently used experimentally.

The potential sequence corresponding to SCV technique is a staircase potential of the form [2, 24]:

$$E_m = E_{initial} + (m-1)\Delta E; \quad 1 \leq m \leq p \quad (4)$$

with p being the total number of potential steps and ΔE the pulse amplitude, whereas the potential sequence corresponding to SWV can be described by the following equation:

$$\left. \begin{aligned} E_p &= E_{initial} + \left[\text{Int} \left(\frac{p+1}{2} \right) - I \right] |\Delta E_s| + (-I)^{p+1} |E_{SW}|; \quad p = 1, 2, \dots, np/2 \\ E_p &= E_{np-p+1}; \quad p = (np/2) + 1, \dots, np \end{aligned} \right\} \quad (5)$$

where $|\Delta E_s|$ is the potential step in the staircase and $|E_{SW}|$ is the square wave amplitude, in agreement with the scheme given in references [15, 16, 25, 26]. The waveform can be applied in single (direct scan only) or cyclic mode (direct and inverse scans). In the latter, once the final potential has been reached, the waveform is reversed, returning through the same sequence of pulses to the initial potential.

The signal is measured at the end of each potential pulse and the net response is the difference between the signal corresponding to a pulse with odd index (forward) and the signal of the following pulse with even index (reverse). Typically, this signal is the current, such that the usual $I_{SW} - E$ square wave voltammetry curve is defined as:

$$I_{SW} = I_{2p-1} - I_{2p} = I_f - I_r; \quad p=1, 2, \dots, (np/2) \quad (6)$$

The subindexes f and r in the above expression refer to the forward and reverse pulses (equal to $2p-1$ and $2p$, respectively).

I_{SW} signal is plotted versus the index potential, defined as an intermediate potential value between each pair of consecutive pulses,

$$E_{index,p} = E_p + (-I)^p |E_{SW}| \quad (7)$$

In order to corroborate these Equations, we have analyzed the experimental behaviour of azobenzene monolayers in aqueous medium on a mercury electrode surface. Azobenzene/hydrazobenzene is a well-known redox couple where both components are strongly adsorbed on a mercury electrode surface. The redox transformation in this medium involves an electrochemically quasi-reversible exchange of two electrons and two protons. This redox reaction is widely used for illustrations of different theoretical models, such as surface redox processes, and electrode reactions with coupled adsorption phenomena in general [20, 21, 27, 28].

Fig. (1) shows the experimental (white circles) and theoretical (solid lines) $I_{SW} - E$ curves corresponding to the system azobenzene 30 μM + 0.5 M KNO₃ (pH=4.28) (simple charge transfer process) obtained in CSWV, for $\tau = 10$ ms and for different values of E_{SW} .

The $I_{SW} - E$ curves of Fig. (1) show that the cathodic and anodic peaks are almost symmetrical and practically centred on the formal potential (dotted line). Note that the $I_{SW} - E$ curves present a single peak for low values of E_{SW} , that becomes into two peaks as E_{SW} increases. Moreover, the separation between them increases with E_{SW} . The characteristic of peak features observed in this Figure informs us that the electrochemical transfer process is quasi-reversible [16].

We have also included different theoretical curves (solid lines) calculated by using Eqs. (1) and (6). Once we

determined the formal potential $E^0 = (-0.123 \pm 0.002)$ V vs SCE. (dotted line), the best fittings were obtained by using the following parameters: $k^0 = (19 \pm 2)$ s⁻¹, $n = 2$, $\alpha = 0.5$ and $Q_{MAX} = 0.110 \pm 0.03$ μ C.

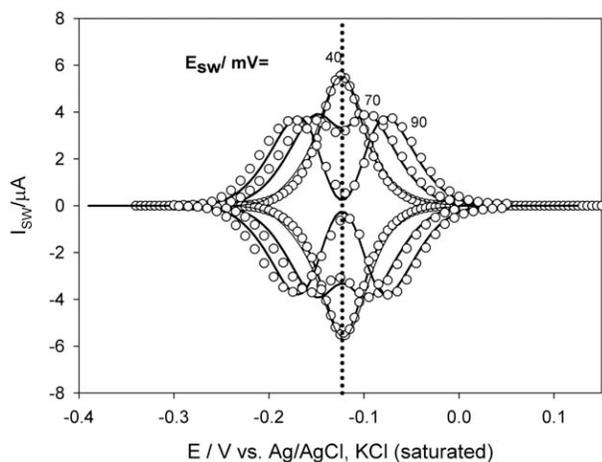
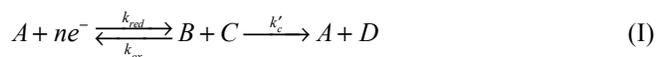


Fig. (1). (white circles) Experimental $I_{SW} - E$ curves corresponding to the system azobenzene 30μ M + 0.5 M KNO_3 pH=4.28 (E mechanism) on a mercury electrode of radius $r_0 = 0.02$ cm. $\tau = 10$ ms. The values of the E_{SW} are on the curves (in mV). (solid lines) Theoretical $I_{SW} - E$ curves calculated for a simple charge transfer process (Eqs. (1) and (6)) by using the following parameters: $E^0 = -0.123$ V, $k^0 = 19$ s⁻¹, $n = 2$, $\alpha = 0.5$, $Q_{MAX} = 0.110$ μ C and $T = 298$ K. Dotted line marks the formal potential position.

3.2. Catalytic Mechanism at a Modified Electrode

We will now consider the study of the electrochemical response of an electrocatalytic process taking place at a modified redox mediator in agreement with the Scheme:



where A and B refer to strongly adsorbed species and C and D to species in solution. The catalytic rate constant is $k_c = k'_c c_C^*$ where k'_c is the true chemical rate constant and c_C^* is the surface concentration of C species, which is considered as constant and equal to the bulk concentration.

The expression of the current-potential curves in staircase voltammetry, for any reversibility degree of the charge transfer of the electrocatalytic process, is given by [19]:

$$\frac{I_p}{Q_{MAX}} = - (k_{T,p} - k_c) \sum_{j=1}^{p-1} \left(\frac{k_{red,j}}{k_{T,j}} (1 - \theta_j) \prod_{l=j+1}^p \theta_l \right) + \frac{k_{red,p}}{k_{T,p}} (k_{T,p} - k_c) \theta_p + k_c \frac{k_{red,p}}{k_{T,p}} \quad (8)$$

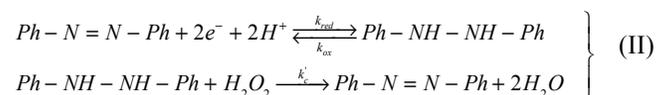
where

$$k_{T,p} = k_{E,p} + k_c \quad (9)$$

$$\text{and } \theta_p = \exp(-k_{T,p} \tau)$$

Note that we obtain the current-potential curves in square wave voltammetry by introducing Eq. (8) in (6).

In this paper, the redox reaction of azobenzene was also investigated in the presence of hydrogen peroxide as oxidizing agent. Hydrazobenzene, formed by electrochemical reduction of azobenzene, is reoxidized by hydrogen peroxide, and the whole electrode reaction turns into a surface catalytic mechanism in according to the next scheme [19, 27]:



In Fig. (2) we have plotted the experimental (circles) and theoretical (solid lines) $I_{SW} - E$ curves corresponding to the system azobenzene 30μ M + 0.5 M KNO_3 + 0.1 M Citric acid/sodium citrate without H_2O_2 (white circles) (E mechanism) and with 25 mM H_2O_2 (black circles) (catalytic mechanism) (pH=3.22). All these curves have been obtained for the same time $\tau = 1.0$ ms. In the CSWV curves we have used different square wave pulse amplitudes E_{SW} which are indicated in the figure.

The $I_{SW} - E$ curves for the catalytic mechanism in Fig. (2, black circles) present a single peak for low values of E_{SW} , which split in two as E_{SW} increases, and also the separation between them is higher with E_{SW} . The peak heights of these curves are almost double those obtained for the E process (white circles) (see Fig. 1).

The formal potential (dotted line) for a catalytic process does not differ from that corresponding to the simple charge transfer reaction. Note that, the different value of the formal potential of Figs. (1, 2) is due to the different conditions of them. The lower pH value in Fig. (2) gives rise to a more anodic value of formal potential, and also to a higher reversibility as we will see below.

We have also included different theoretical curves (solid lines) calculated from Eqs. (1), (6) and (8). Once the formal potential $E^0 = (-0.0715 \pm 0.0015)$ V vs SCE. (dotted line) was determined, the best fittings were obtained with the following parameters: $k^0 = 480$ s⁻¹, $n = 2$, $\alpha = 0.5$ and $Q_{MAX} = 0.0159 \pm 0.001$ μ C being $k_c = 1$ s⁻¹ for the catalytic curves.

In Fig. (3) we have studied the effect of the sweep rate v on the experimental $I - E$ curves in CSCV corresponding to the system azobenzene 30μ M + 0.5 M KNO_3 + 0.1 M Citric acid/sodium citrate without H_2O_2 (white circles) (E mechanism) and with 100 mM H_2O_2 (black circles) (catalytic mechanism) (pH=3.22), respectively, in CSCV with $\Delta E = 5$ mV.

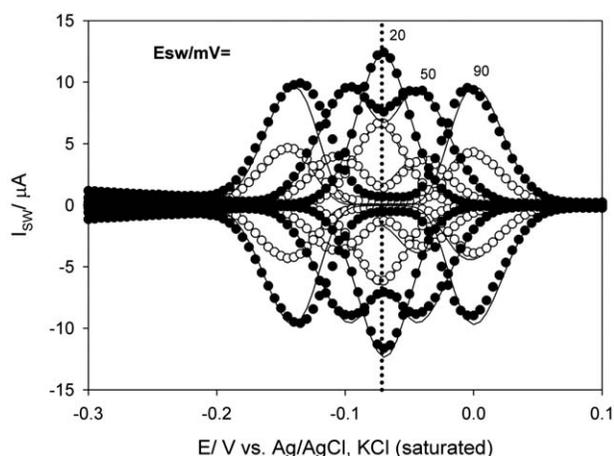


Fig. (2). Experimental $I_{SW} - E$ curves corresponding to the system azobenzene $30 \mu M + 0.5 M KNO_3 + 0.1 M$ Citric acid/sodium citrate without H_2O_2 (simple charge transfer process) (white circles) and with $25 mM H_2O_2$ (black circles) (electrocatalytic process) (pH=3.22) adsorbed on a mercury electrode of radius $r_0 = 0.02 cm$. $\tau = 1.0 ms$. The values of the square wave pulse amplitude E_{SW} (in mV) are on the curves. (solid lines) Theoretical $I_{SW} - E$ curves (Eqs.(1), (6) and (8)) calculated by using the following parameters: $k^0 = 480 s^{-1}$, $E^0 = -0.0715 V$, $n = 2$, $Q_{MAX} = 0.0159 \mu C$ and $T = 298 K$ being $k_c = 1 s^{-1}$ for the catalytic curves. Dotted line marks the formal potential position.

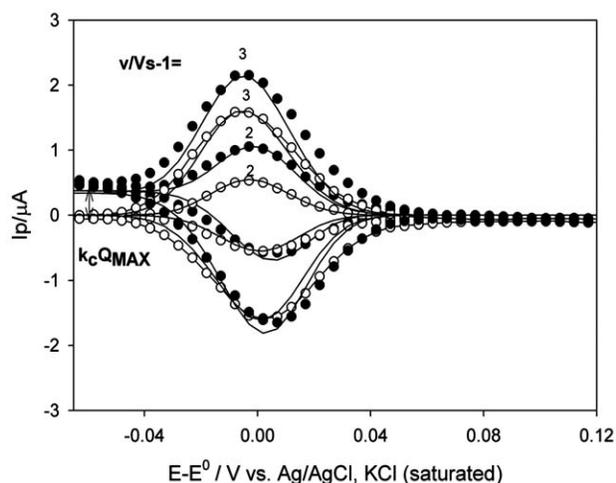


Fig. (3). Experimental $I - E$ curves in CSCV corresponding to the system azobenzene $30 \mu M + 0.5 M KNO_3 + 0.1 M$ Citric acid/sodium citrate without H_2O_2 (simple charge transfer process) (white circles) and with $100 mM H_2O_2$ (black circles) (electrocatalytic process) (pH=3.22) adsorbed on a mercury electrode of radius $r_0 = 0.02 cm$. $\Delta E = 5 mV$. The values of sweep rate ν (in Vs^{-1}) are on the curves. (solid lines) Theoretical $I - E$ curves (Eqs. (1) and (8)) calculated by using the following parameters: $k^0 = 480 s^{-1}$, $n = 2$, $Q_{MAX} = 0.078 \mu C$ and $T = 298 K$ being $k_c = 4 s^{-1}$ for the catalytic curves.

From the curves in Fig. (3) it can be seen that in both mechanisms the decrease of the sweep rate ν leads to a decrease of the current. Nevertheless, for the catalytic mechanism the peak heights are higher than those of an E mechanism and also the current reaches the value $k_c Q_{MAX}$ at cathodic potentials, independently of the sweep rate [19, 29].

To check the goodness of the data obtained from the experimental $I - E$ curves we have included in Fig. (3) the theoretical ones obtained in CSCV, calculated from Eqs. (1) and (8), which correspond to a simple charge transfer process and a catalytic process, respectively (solid lines). By taking into account the charge transfer constant obtained in the same conditions ($k^0 = 480 s^{-1}$), the theoretical curves have been calculated using the following parameters: $n = 2$, $\alpha = 0.5$, $Q_{MAX} = 0.078 \mu C$ and being $k_c = 4 s^{-1}$ for the catalytic mechanism. The agreement between theoretical and experimental results confirms the accuracy of the experimental parameters deduced. From the value of k_c used, we can finally obtain that the true chemical rate constant of the mechanism is $k_c' = 40 M^{-1} s^{-1}$ [19].

4. CONCLUSIONS

The experimental study of Azobenzene+ H_2O_2 system with the multipulse potential techniques CSCV and CSWV has led to check analytical and explicit expressions previously deduced by us and to obtain electrochemical and chemical information of this system in a very simple way.

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