Detection of interaction between redox centers of surface confined molecules by means of Cyclic Voltammetry and Differential Staircase Voltcoulommetry

J. González, A. Molina *, C.M. Soto, C. Serna

Departamento de Química Física, Universidad de Murcia, Espinardo 30100, Murcia, Spain

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ABSTRACT

Analytical expressions for the reversible electrochemical response of surface confined molecules with dependent or independent redox centers to Cyclic Voltammetry (CV, I–E curves) and Differential Staircase Voltcoulommetry (DSVC, dQ/dE–E curves), are presented and compared. The terms dependent and independent centers refer to those which are located inside the molecule at distances smaller or greater than a typical molecular diameter, respectively. In the case of dependent redox centers (stepwise processes), easy methods for characterising their intramolecular repulsive or attractive interactions are given. DSVC curves allow an effective de-coupling of the non-faradaic components of the response due to the discrete nature of the potential waveform used.

Simple criteria for analyzing surface dependent and independent redox centers are given and experimentally tested obtaining surface coverages and the formal potential of each electroactive center.

1. Introduction

The electrochemical response of molecules with multiple electroactive centers is governed by both diffusive flux and the degree of interaction between centers within each molecule. The systems are described by a sequence of redox steps, irrespective of the degree of interaction between the redox centers [1–5]. On the other hand, when multicenter redox molecules are strongly adsorbed to the electrode surface forming an electroactive monolayer, two types of responses depending on the separation between the redox centers can be distinguished:

(a) Adsorbed molecules with “dependent” redox centers: In this case the different centers are located inside the molecule at distances smaller than a typical molecular diameter. This situation can be described by a stepwise charge transfer with separate or superimposed responses, depending on the degree and nature of the interaction between the redox centers which is determined by the difference between their formal potentials. Small adsorbed molecules such as quinones or mononucleotides like flavin are among the species which present this behaviour [6–10]. In this case the intramolecular interaction between the centers can be attractive or repulsive depending on the value of the difference between their redox potentials.

(b) Adsorbed molecules with “independent” redox centers: In this situation, the molecules present two or more electroactive centers, separated from each other by a fixed distance greater than a typical molecular diameter (in the range of nanometers). In this case, the interaction between the redox centers is negligible whatever the difference between their formal potentials. Metalloproteins such as ferredoxin, which contains two FeS clusters located about 1.2 nm apart [11,12], are examples of this type of molecules. Note that this response is equivalent to that of independent and non interacting adsorbed species at electrode surface.

The electrochemistry of these surface confined multicenter redox molecules has attracted considerable effort in recent years, in the attempt to resolve the different faradaic processes taking place, especially those related with biomolecules, such as metalloproteins [10,13–15], enzymes [6,10,13–15], and oligonucleotides [10,15], among others. This interest is based on the fact that the attachment of these molecules gives rise to a wide range of applications of the resulting structures, including molecular electronics, electrocatalysis, nanodevices and bioelectronics [6,7,16–19]. In addition, immobilisation of these molecules has provided a convenient way for fundamental studies concerning electron transfer between a redox center placed at a well-defined distance from the electrode surface in the absence of other effects derived from the presence of mass transport [20,21].

In this context, electrochemical techniques, especially Cyclic Voltammetry, have proved to be useful tools for obtaining a better understanding of the processes taking place [6,15,22]. The study of...
charge transfer reactions with adsorbed species in Cyclic Voltammetry (CV) was developed by Laviron [23], who deduced simple methods for the analysis of these systems [23,24]. Nevertheless, CV also presents disadvantages for studying surface redox processes, mainly derived from complex double layer influences associated to the $I-E$ response [25–28], and low faradaic-to-background ratios observed when monolayers of biomolecules are considered [10,12,15]. These non-idealities of CV are responsible for the low agreement between theory and experiments observed with this technique.

One interesting alternative to CV is the use of multipotential steps techniques such Square Wave Voltammetry or Staircase Volta- tammery, for which signals with improved faradaic-to-back- ground ratio which are much less affected by double layer influences can be recorded [29–31]. However, these techniques lead to null current values when the charge transfer processes are reversible [28].

In order to overcome this limitation, we introduced in a previ- ous paper a new electrochemical technique called Differential Staircase Voltacoulometry (DSVC) which leads to an easily characterisable peak shaped response for reversible charge transfer reactions [32]. The charge is a useful variable in the study of redox monolayers since, in the case of fast charge transfers, the charge–potential relationship is independent of the electrochemical tech- nique from which it has been obtained and allows a very simple and effective elimination of the non-faradaic component of the response [32–36].

In this paper we present simple analytical expressions for the charge–potential $(Q-E)$ curve and its differential $(dQ/DE=E)$ cor- responding to multcenter redox molecules with independent and dependent redox centers. We have compared the responses of these species obtained in DSVC and in Cyclic Voltammetry and we have demonstrated that, for reversible processes, the Cyclic Voltammetric curves divided by the scan rate and the Differential Staircase Voltcoulometric curves should be coincident. This fact has been used as reversibility criteria in this paper.

We have carried out a quantitative analysis to obtain the char- acteristic parameters of the charge transfers under study. Simple criteria for diagnosing each type of surface process are given and experimentally tested with three different systems: (a) 9,10-Phe- nantrenequinone adsorbed at a mercury electrode, (b) A molbyde- num polyoxometalate, adsorbed at a glassy carbon electrode, (c) A mixture of the sodium salts of 9,10-antraquinone 2,6 disulfonic acids at mercury electrode, whose $(dQ/DE=E)$ responses correspond to molecules with two dependent redox centers with superimposed and separate signals (cases a and b, respectively), and two independent charge transfers with a single signal (system c). In all the cases the agreement obtained between theoretical and experimental re- sponses was very good.

2. Experimental section

2.1. Reagents and chemicals

$\text{Mo}_{12}\text{Na}_{3}\text{O}_{40}\text{P}$ (MO), $\text{HClO}_4$, $\text{NaH}_2\text{PO}_4$, $\text{Na}_2\text{HPO}_4$ (Merck), 9,10-Phenantrenequinone (PQ), 9,10-antraquinone 2,6-disulfonic acid disodium salt (AQDS), methanol (Sigma–Aldrich) and antraquinone-2 sulfonic acid sodium salt (AQS) (Fluka) were reagent grade and used as received.

Monolayers of MO at glassy carbon electrode were formed from an aqueous 1 $\mu$M solution in 0.1 M $\text{HClO}_4$, by applying a rest potential of 0.6 V vs. SCE for 1 s prior to measurements.

PQ was dissolved in methanol, then diluted with aqueous phos- phate buffer solutions (PBS) until the final concentration was 1 $\mu$M.

PQ monolayers were formed at the mercury surface at a rest poten- tial of $E = -0.4$ V vs. silver/silver chloride reference for 100 s under stirring prior to measurements.

AQDS and AQS were dissolved in water, then diluted with $\text{HClO}_4$ solutions until the final concentration of each quinone was 10 $\mu$M. Both were adsorbed at the mercury surface at a rest potential of $E = -0.4$ V vs. silver/silver chloride reference for 10 s under stirring prior to measurements.

The low concentrations used for the different electroactive spe- cies guarantee that any possible contribution to the whole re- sponse due to dissolved species can be considered negligible. Moreover, we have checked that desorption has not taken place in the time scale of the experiments by comparing CV responses of the freshly prepared monolayer and after a series of essays.

2.2. Electrochemistry

Differential Staircase Voltacoulometry (DSVC) and Cyclic Volt- tammery (CV) were performed using a home made computer-dri- ven potentiosstat–galvanostat.

A three-electrode cell (with a glassy carbon electrode of diame- ter 0.3 cm from CH Instruments as working electrode), and a home made static mercury drop electrode (radius 0.02 cm) were em- ployed in the experiments. The counter electrode was a Pt foil, and the reference electrodes were a saturated calomel electrode (SCE) or Ag/AgCl, KCl (sat.). 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 measure- ments, with nitrogen atmosphere maintained over the solution during all the experiments.

The glassy carbon electrode was mechanically polished on alu- mina slurry (0.05 $\mu$m, Buehler), washed and electrochemically cleaned by cycling the potential between 0 V and $-1.4$ V (vs. SCE) in 2.0 M NaOH and then between 1.6 V and 0.4 V (vs. SCE) in 1.0 M $\text{H}_2\text{SO}_4$ until a stable voltammogram was obtained. It was then washed with ethanol and water.

In the case of the monolayer of the mixture of the sodium salts of 9,10-antraquinone 2,6 disulfonic and 9, 10-antraquinone 2 sul- fonic acids at mercury electrode, the non-faradaic contribution to the response gives rise to a practically constant baseline (i.e., a po- tential independent double layer capacitance) which has been sub- tracted from the whole response. In the case of the PQ monolayer at mercury and of the MO monolayer at glassy carbon electrode, the baseline was adjusted to a polynomial of third degree and then subtracted by means of the Transforms routines of SigmaPlot 10.0 for Windows. The half peak width of the different responses, de- fined as the potential separation observed for two signal values equal to the half peak height, has been measured on the corrected voltammograms or voltacoulomgrams.

We have selected low values of the scan rate in CV for the three experimental systems studied in order to obtain electrochemically reversible responses.

3. Theory

3.1. Surface confined molecules with “dependent” redox centers

In this section, we will consider a stepwise mechanism which takes place in an electroactive monolayer of molecules containing dependent redox centers. This situation can be described by Scheme 1 corresponding to $k$ successive charge transfer steps, in which species $Q_i$ ($i = 1, 2, \ldots, k+1$) refers to the different redox states of adsorbed molecule $Q$, and $E^\text{sw}$ to the formal potential of step $i$ ($1, 2, \ldots, k$).
Although the current is null for any reversible step, the trans-
potential step voltamperrerometric techniques in this case.

Under these conditions, the following assumptions are fulfilled for
any potential pulse

$$I_i = \frac{dQ_{i}}{dt} = 0 \quad i = 1, 2, \ldots, k$$

(7)

In agreement with Eq. (7), the current associated to fast charge
transfer cannot be measured and therefore it is not possible to use
potential step voltamperrerometric techniques in this case.

We assume that the adsorption follows the Langmuir isotherm, that
deterogeneity of the electroactive monolayer can be ignored and
that no desorption takes place in the time scale of the experiment.

The total excess $\Gamma_T$ is constant during the whole experiment:

$$\Gamma_T = \sum_{i=1}^{k+1} \Gamma_0_i$$

(1)

$$\Gamma_T = \Gamma_0_i(0) \quad \Gamma_0_i(0) = 0: \quad i = 2, 3, \ldots, k + 1$$

(4)

By combining Eqs. (1), and (2) we have:

$$\Gamma_0_i = \frac{Q_{i}}{Q_M} \Gamma_0_i$$

(2)

with

$$\eta_i = \frac{F}{RT}(E - E_i^o)$$

(3)

We also assume that the adsorbed molecule is totally oxidised
at the beginning of the experiment, i.e., $O_i$ is the only species ini-
itially present in the electrode surface, so at $t = 0$

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$$\Gamma_0_i = \frac{Q_{i}}{Q_M} \Gamma_0_i$$

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$$\eta_i = \frac{F}{RT}(E - E_1^o)$$

(3)

Eq. (10) is valid for any multicenter molecule with dependent cen-
ters (i.e., two step process or EE process, $k = 2$), Eq. (10) simplifies to:

$$\frac{Q}{Q_M} = \frac{2K + J}{K + J + J^2}$$

(11)

with

$$J = \exp \left( \frac{F}{RT}(E - E_i^o) \right)$$

(12)

$$K = \exp \left( \frac{F}{RT}(E - E_{i-1}^o) \right)$$

(13)

$$\Delta E_i^o = (E_{i-1}^o - E_i^o)$$

(14)

Then, the expression for the total transformed charge of a process with
$k$ independent steps is given by:

$$\frac{Q}{Q_M} = \sum_{i=1}^{k+1} \frac{1}{1 + e^\eta_i}$$

(6)

From Eqs. (5), and (6) it can be concluded that, under these con-
ditions, the surface concentrations of the different species are con-
stant for a given potential pulse $E$ such that the current for the ith
step is given by [28,32]:

$$I_i = \frac{dQ_{i}}{dt} = 0 \quad i = 1, 2, \ldots, k$$

(7)

In agreement with Eq. (7), the current associated to fast charge
transfer cannot be measured and therefore it is not possible to use
potential step voltamperrerometric techniques in this case.

Although the current is null for any reversible step, the trans-
formed charge for the ith step is not null [32], and the expression of
$Q_i(= \int_i^\tau I_i dt$ with $\tau$ being the time length of the potential pulse) is given by:

$$\frac{Q_i}{Q_M} = \left[ 1 - \sum_{i=1}^{k+1} \frac{\Gamma_0_i}{\Gamma_T} \right] i = 1, 2, \ldots, k$$

(8)

with

$$Q_M = FA \Gamma_T$$

(9)

where $A$ is the electrode area.

The transformed normalised charge for a process of $k$ steps is the
sum of all the charges transformed and is given by (Eqs. (5),
(6), and (8)),

$$\frac{Q}{Q_M} = \sum_{i=1}^{k} \frac{Q_{m_i}}{Q_M} = \frac{k + \sum_{i=1}^{k+1} \left( \sum_{i=1}^{k+1} e^{\eta_i} \right)}{1 + \sum_{i=1}^{k+1} \prod_{i=1}^{k+1} e^{\eta_i}}$$

(10)

For the particular case of a molecule with two dependent redox centers
(i.e., two step process or EE process, $k = 2$), Eq. (10) simplifies to:

$$\frac{Q}{Q_M} = \frac{2K + J}{K + J + J^2}$$

(11)

with

$$J = \exp \left( \frac{F}{RT}(E - E_1^o) \right)$$

(12)

$$K = \exp \left( \frac{F}{RT}(E - E_2^o) \right)$$

(13)

Eq. (10) is valid for any multicenter molecule with dependent cen-
ters whatever the difference between the formal potentials of the same.

### 3.2. Surface confined molecules with “independent” redox centers

In this section, we will obtain the expression for the total trans-
formed charge corresponding to the reduction of an adsorbed mole-
cule with $k$ independent reversible redox centers. This response is
equivalent to that of $k$ independent and non interacting species ad-
orsed at the electrode surface, and is described by Scheme 2, in
which $O_1, O_2, \ldots, O_k$ denote the $k$ independent centers of the
adsorbed molecule or the $k$ independent species.

In this case we assume that the maximum excess of the $O_i/R_i$
moiety, $\Gamma_0_i + \Gamma_k = \Gamma_i$, is the same for $i = 1, 2, \ldots, k$, and also that
the Nernstian condition holds for all the centers

$$\Gamma_0_i = e^{\eta_i} \Gamma_k$$

with

$$\eta_i = \frac{F}{RT}(E - E_i^o)$$

(3)

Thus, the expression for the total transformed charge of a process with
$k$ independent steps is given by:

$$\frac{Q}{Q_M} = \sum_{i=1}^{k} \frac{1}{1 + e^\eta_i}$$

(6)

In the particular case of two independent centers (two independent
$E$ processes), Eq. (14) becomes:

$$O_i + e^- \rightarrow R_i \quad E_i^o$$

$$O_j + e^- \rightarrow R_j \quad E_j^o$$

$$\vdots$$

(II)

$$O_i + e^- \rightarrow R_i \quad E_i^o$$

$$O_j + e^- \rightarrow R_j \quad E_j^o$$

$$\vdots$$

$$O_k + e^- \rightarrow R_k \quad E_k^o$$

(III)

Scheme 2.
with $J$ and $K$ given by Eqs. (12) and (13), respectively. Note that in this case, we have denoted $Q_m = \text{FA} \tau$.

3.3. Differential Staircase Voltcoulommetry

We will consider in this paper the technique called Differential Staircase Voltammetry (DSVC), in which a staircase potential of constant pulse amplitude $\Delta E = E_{m+1} - E_m (1 \leq m \leq (p-1))$ is applied. The potential corresponding to any step of the whole sequence is given by

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

(16)

The signal corresponding to Differential Staircase Voltammetry is built by measuring the charge at the end of each potential pulse applied and plotting the difference between the charge corresponding to two consecutive potential pulses, $E_m$ and $E_{m-1}$.

$$\Delta Q = (Q_m - Q_{m-1})$$

(17)

vs. the applied potential $E_m$ [32] as it can be seen in Scheme 3.

It is convenient to divide $\Delta Q$ by the pulse amplitude $\Delta E$ in order to obtain the $(\Delta Q/\Delta E) - E$ response. Note that the cyclic voltammetric curve $(F^V - E)$ coincides with the $(\Delta Q/\Delta E) - E$ one for a reversible process when $\Delta E \ll RT/F$ [32], i.e.:

$$\frac{\Delta Q}{\Delta E} \approx \frac{dQ}{dE} = \frac{F}{RT} \left( K + J \right) \quad \Delta E \ll 10 \text{ mV}$$

(18)

with $\gamma$ being the sweep rate.

Thus, in the simpler case of a molecule with two dependent redox centers, Eq. (18) can be written as (see Eq. (11)):

$$\left[ \frac{d(Q/Q_s)}{dE} \right]_{\text{dependent centers}} = \frac{F}{RT} \left( KJ + 4J^2 + J^3 \right)$$

(19)

whereas in the case of a molecule with two independent redox centers Eq. (18) takes the form (see Eq. (15)):

$$\left[ \frac{d(Q/Q_s)}{dE} \right]_{\text{independent centers}} = \frac{F}{RT} \left[ \frac{J}{(1 + J)^2} + \frac{KJ}{(1 + KJ)^2} \right] $$

(20)

Eq. (19) coincides with those previously reported by Laviron et al. [24] and Kano and Uno [8] for Cyclic Voltammetry.

4. Results and discussion

For the sake of simplicity we will focus the discussion on the theoretical and experimental responses of adsorbed molecules with two dependent or independent centers (i.e., EE process or two independent E processes), although Eqs. (10) and (14) are applicable to any number of centers in the adsorbed molecules.

4.1. Theoretical results

In Fig. 1 we have compared the theoretical $(Q/Q_s)$ vs. $E$ (a and b) and $d(Q/Q_s)/dE$ vs. $E$ (c and d) curves obtained for a molecule with two dependent (a and c) or independent (b and d) redox centers, calculated from Eqs. (11), (19) and (15), (20), respectively, for different values of the parameter $\Delta E^0 = (E^0 - E^0)$. In the case of a molecule with dependent centers (a and c), the responses obtained for very negative values of $\Delta E^0$ (i.e., normal ordering of potentials, see [5]), show two well defined monoelectronic signals (sigmoidal waves for the charge, Fig. 1a, and peaks for its differentiation, Fig. 1b). These curves evolve towards a single signal as $\Delta E^0$ increases. When the potential of the second step is much more negative than that of the first, two clearly separate responses corresponding to each step are obtained, indicating that the intermediate species ($O_2$ in the second step of Scheme 2) is stable in a wide range of potentials. In the contrary case, i.e., for $\Delta E^0 \geq -70 \text{ mV}$ (potential inversion, i.e., the introduction of the second electron occurs with greater facility than the first [5]), a single $Q$ vs. $E$ (Fig. 1a) or $(dQ/dE)$ vs. $E$ curve (Fig. 1b) is obtained. Under these conditions, the half wave potential of curves in Fig. 1a, which coincides with the peak potential of curves in Fig. 1b, is equal to $(E^0 + E^0)/2$. Finally, for $\Delta E^0 \geq 140 \text{ mV}$, the responses corresponding to a molecule with two dependent redox centers become indistinguishable from that corresponding to a simple charge transfer of two electrons.

Concerning the responses obtained for molecules with independent centers (b and d), they present a symmetrical behaviour with $\Delta E^0$. So, for high values of $|\Delta E^0|$, two clearly separated waves (Fig. 1b) or peaks (Fig. 1d) are observed, whereas for $140 \leq \Delta E^0 \leq 140 \text{ mV}$ partially or totally superimposed responses are obtained. Note that $(dQ/dE)$ vs. $E$ curves for independent centers shown in Fig. 1d have a symmetry axis at the potential.
to that corresponding to dielectronic process (\(\text{dQ/QM}\) vs. \(E-E_1^0\)) and \(\Delta E^0\) (in mV) are on the curves. \(E_1^0 = 0\) V, \(T = 298.15\) K. We have plotted the absolute values of the derivative curves.

\(\text{dQ/QM} = 0\), black dot in Fig. 2a and b), for which \(W_{1/2}\) is the same as that corresponding to a simple monoelectronic charge transfer (90 mV), although the response has a double intensity (compare solid and dashed lines in Fig. 2c). This particular case corresponds to absence of interactions between the dependent redox centers, in accordance with the results previously reported for solution soluble multicenter redox molecules in any electrochemical technique and for any electrode geometry [1–3].

In the case of two independent redox centers, \(W_{1/2}\) varies in the opposite way when \(\Delta E^0 < 0\) than when \(\Delta E^0 > 0\). In the former case, this variation is coincident with that obtained for a molecule with two dependent redox centers \((\Delta E^0 < 70\) mV). Note that when \(\Delta E^0 = 0\), \(W_{1/2}\) again takes the value corresponding to a single charge transfer reaction.

These dependences of the peak height and half peak width on \(\Delta E^0\) can be analytically treated. In the case of dependent centers, by making the differentiation of Eq. (19) zero, a fourth degree polynomial in \(J\) is obtained, for which the following three real positive roots for \(J\) are obtained:

\[(\Delta E^0)^2 + \Delta E_1^0 + \Delta E_2^0)/2\] and also that they are totally coincident with those of molecules with dependent centers for very negative values of \(\Delta E^0\) (see above).

Fig. 2 shows the evolution of peak height \((h_{\text{peak}}, \text{Fig. 2a})\) and half peak width \((W_{1/2}, \text{Fig. 2b})\) of the \((\text{dQ/dE})\) vs. \(E\) curves with \(\Delta E^0\), corresponding to a molecule with two dependent (solid lines) or independent (dotted lines) redox centers.

From Fig. 2a we can observe that in the case of dependent centers the peak height increases with \(\Delta E^0\) from the value corresponding to a monoelectronic charge transfer \((F/4RT)Q_{\text{re}})\) [32] up to that corresponding to dielectronic process \((F/RT)Q_{\text{re}}\). In the case of two independent redox centers (dotted lines) this peak height is coincident with that corresponding to a simple charge transfer for \(|\Delta E^0| < 140\) mV, taking higher values for intermediate values of \(\Delta E^0\) \((-140 < \Delta E^0 < 140\) mV) and reaching its maximum for \(\Delta E^0 = 0\).

Fig. 2b shows that the half peak width for a molecule with two dependent redox centers (solid lines) takes the value 90 mV (monoelectronic charge transfer reaction) when two separate mono-electronic peaks are obtained \((\Delta E^0 < -140\) mV), showing a sharp jump at \(\Delta E^0 = -140\) mV (corresponding to the case at which the height of the central valley coincides with the half peak height). For \(\Delta E^0 > -140\) mV, a partially or totally superimposed response is obtained and \(W_{1/2}\) decreases with \(\Delta E^0\) until it reaches the value of 45 mV, corresponding to a dielectronic charge transfer reaction. A special case is to \(\Delta E^0 = -35.6\) mV \((K = 1/4,\) black dot in Fig. 2a and b), for which \(W_{1/2}\) is the same as that corresponding to a simple monoelectronic charge transfer (90 mV), although the response has a double intensity (compare solid and dashed lines in Fig. 2c). This particular case corresponds to absence of interactions between the dependent redox centers, in accordance with the results previously reported for solution soluble multicenter redox molecules in any electrochemical technique and for any electrode geometry [1–3].
The first root ($J_1$) is valid for any $\Delta E^0$ value and corresponds to the following applied potential (see Eqs. (12), (13) and (21a)):

$$E_1 = \left(\frac{E_0^1 + E_0^2}{2}\right)$$

(22)

The physical meaning of $J_1$ depends on the $K$ value considered. For $K > 0.06$ ($\Delta E^0 > -70$ mV) (superimposed responses), it corresponds to the peak potential of the single response obtained (see Fig. 3). In this case the peak height $h_{peak}$ is given by (see Eqs. (19) and (21a)),

$$h_{peak} = \frac{F}{RT} Q_M \frac{2\sqrt{K}}{1 + 2\sqrt{K}}$$

(23)
which coincides with that obtained by Lavieron for Cyclic Voltammetry (see Eq. (21) in [37]). For $\Delta E^\theta < -70$ mV ($K < 0.06$, separated peaks), $J_1$ corresponds to the potential of the minimum between both peaks (see Fig. 3b and c).

The values of the peak potentials $E_2$ and $E_3$ are deduced from those of $J_1$ and $J_3$ (see Eqsns. (12) and (21b-c)), and the peak heights tend to $(F/4 kT)Q_m$ as $\Delta E^\theta$ decreases.

The half peak width $W_{1/2}$ when a single peak is observed is given by (see Eqs. (19) and (23)):

$$W_{1/2} = \frac{2RT}{F} \ln \left[ B + \sqrt{B^2 - 1} \right]$$

with

$$B = \left[ 1 + \sqrt{1 - 4K + 16K \sqrt{k + 32K^2}} \right] / 4K$$

This expression coincides with that obtained by Armstrong et al. [38].

For $\Delta E^\theta < -85$ mV Eq. (24) gives rise to errors above 4 mV in the determination of this parameter. This difficulty has been avoided in this paper, since the working curve in Fig. 2b (solid line) can be used for determining this parameter. This difficulty has been avoided in this paper, since the working curve in Fig. 2b (solid line) can be used for determining $\Delta E^\theta$.

In the case of two independent redox centers, by equating the differential of Eq. (20) to zero, the following three real positive solutions are obtained:

$$J_1 = \sqrt{k}$$  \hspace{2cm} (a) any value of $K$

$$J_2 = -\frac{6K + 1}{2(1 - K)} \sqrt{k}$$  \hspace{2cm} (b) $K < 0.07 (\Delta E^\theta > 70$ mV

$$J_3 = -\frac{6K + 1}{2(1 - K)} \sqrt{k}$$  \hspace{2cm} (c) $K > 14 (\Delta E^\theta > 70$ mV

For $(70 < \Delta E^\theta < 70)$ mV the potential corresponding to the first root, $J_1$ is the peak potential and it is also given by Eq. (22). In these conditions we deduce for the peak height:

$$h_{\text{peak}} = \frac{FRT Q_M}{\sqrt{\left( \frac{1}{1 + \sqrt{k}} \right)^2 + \frac{K \sqrt{k}}{1 + \sqrt{k}}}^2}$$

From this expression it can be easily deduced that the maximum peak height corresponds to $K = 1$ ($\Delta E^\theta = 0$) with $h_{\text{peak}} = (FQ_M/2RT)$, i.e., twice that corresponding to a single charge reaction and coincident with that obtained for a molecule with dependent and non interacting centers ($\Delta E^\theta = -35.6$ mV, see above).

For $|\Delta E^\theta| > 70$ mV, two separate signals are obtained, and in agreement with Fig. 2 (dotted lines), the two peak heights tend to that corresponding to a single charge transfer. Concerning the half peak width, no simple expression can be obtained from Eq. (19), though it can be reduced in a two electron two proton reversible conversion with these last transfers being not rate limiting according to [8].

In Fig. 4, we have plotted the $(IE/|v|) vs. E$ (solid lines) and $(dQ/|dE|)$ vs. $E$ (white dots) curves corresponding to the application of a linear potential sweep (LSV) and to a staircase potential (DSVC) to a solution 1.0 $\mu$M PQ + 0.1 M phosphate buffer solutions (PBS, pH = 7.2). These curves have been obtained for a scan rate $v = 150$ mV s$^{-1}$ in both techniques.

4.2. Experimental results

We have carried out the experimental verification of the above predictions by analysing the CV and DSVC responses of three systems which give rise to some of the most representative behaviour discussed in Section 4.1. These systems are:

(a) 9,10-Phenantrenoquinone (PQ) in aqueous buffered medium (pH = 7.2) adsorbed at a mercury electrode (molecule with two dependent centers with attractive interactions, Fig. 4).

(b) A molybdenium polyoxometalate, $\text{Mo}_{12}\text{Na}_3\text{O}_{44}^-$ (MO), in aqueous acidic media adsorbed at a glassy carbon electrode (molecule with two dependent centers with repulsive interactions, Fig. 5).

(c) A mixture of the sodium salts of 9,10-antraquinone 2,6 disulfonic and 9, 10-antraquinone 2 sulfonic acids in aqueous medium adsorbed at a mercury electrode (two independent quasi-identical centers which give rise to superimposed signals, Fig. 6).

The structures of these molecules are given in Scheme 4.

We have also checked that the cathodic and anodic peaks of the CV and DSVC curves for all the systems under study are symmetric, so we have focused on the response of the first scan (i.e., Linear Sweep Voltammetry, LSV).

4.2.1. Molecules with two dependent centers with attractive intramolecular interactions

We have analyzed the response of Phenantrenoquinone (PQ) in an aqueous buffered media adsorbed at a mercury electrode as an example of adsorbed molecule with two dependent centers with attractive interactions between both centers (intramolecular interactions, i.e., $\Delta E^\theta > -35.6$ mV). PQ has two carbonyl groups that can be reduced in a two electron two proton reversible conversion with these last transfers being not rate limiting according to [8].

In Fig. 4, we have plotted the $(IE/|v|) vs. E$ (solid lines) and $(dQ/|dE|)$ vs. $E$ (white dots) curves corresponding to the application of a linear potential sweep (LSV) and to a staircase potential (DSVC) to a solution 1.0 $\mu$M PQ + 0.1 M phosphate buffer solutions (PBS, pH = 7.2). These curves have been obtained for a scan rate $v = 150$ mV s$^{-1}$ in both techniques.
In Fig. 5, we have plotted the \( \frac{dQ}{dE} \) vs. \( E \) (solid lines) and \( \frac{dF}{dE} \) vs. \( E \) (white dots) curves calculated from Eqs. (19) (black dots), for a scan rate \( \nu = 1 \text{ V s}^{-1} \). This system also presents a reversible behaviour in line with the superimposition of the experimental \( \frac{dF}{dE} \) vs. \( E \) and \( \frac{dQ}{dE} \) vs. \( E \) curves shown in this figure (we have checked that this superimposition is also observed for different scan rates in the range 0.1–1.0 \text{ V s}^{-1} \). Since MO is the only electroactive species adsorbed, the two peaks observed clearly point to an EE mechanism with separate peaks. Therefore, the position of each peak corresponds to the formal potential of each step and the peak height should be given by \( \Gamma = \frac{F(\nu/4)Q_{\text{Mo}}}{2} \). By using this expression we have obtained \( Q_{\text{Mo}} = 0.58 \mu\text{C} \) and a surface concentration \( \Gamma = 1.9 \times 10^{-10} \text{ mol cm}^{-2} \). We have also included in this figure the theoretical \( \frac{dQ}{dE} \) vs. \( E \) curve for DSCV calculated from Eq. (19) (black dots), for a scan rate \( \nu = 1 \text{ V s}^{-1} \). The system also presents a reversible behaviour in line with the superimposition of the experimental \( \frac{dF}{dE} \) vs. \( E \) and the theoretical \( \frac{dQ}{dE} \) vs. \( E \) curve for DSVC calculated from the following formal potentials: \( E^{\theta}_{\text{PQ}} = -99 \text{ mV} \) and \( E^{\theta}_{\text{PQ}} = -65 \text{ mV} \). The surface concentration of PQ can be determined from the peak height by using Eq. (23), leading to \( Q_{\text{Mo}} = 15.1 \text{ nC} \) (i.e., \( \Gamma_{\text{PQ}} = 3.11 \times 10^{-11} \text{ mol cm}^{-2} \)). This value is far from the maximum coverage for this molecule \( 10^{-10} \text{ mol cm}^{-2} \) [8]), which implies that intermolecular interactions have no significant influence on the \( W_{1/2} \) value and all the theoretical assumptions are fulfilled. An additional verification of this comes from the excellent agreement between the experimental LSV and DSCV curves and the theoretical response calculated from Eqs. (18) and (19) (black dots), by using the experimental values of \( \Delta E^{\theta}_{\text{PQ}} \) and \( \Delta E^{\theta}_{\text{Q}} \) obtained from this figure.

4.2.2. Molecules with two dependent centers with repulsive intramolecular interactions

To illustrate the case of a molecule with two dependent redox centers with repulsive interactions (EE process with separated responses), we have analysed the reduction of the phosphomolybdate heteropolyanion \( \text{Mo}_{12}\text{Na}_3\text{O}_{40}\text{P} \) (MO) at a glassy carbon electrode. This polyoxometallate may present up to four consecutive reductions in HClO\(_4\) 0.1 \text{ M} in agreement with [40], but we will focus our discussion on the two reductions taking place at the potential interval (0.4–0 V).

In Fig. 5, we have plotted the \( \frac{dF}{dE} \) vs. \( E \) (solid lines) and \( \frac{dQ}{dE} \) vs. \( E \) (white dots) curves obtained in LSV and DSCV with a MO monolayer in an aqueous 0.1 M HClO\(_4\) medium, for a scan rate \( \nu = 1 \text{ V s}^{-1} \).

4.2.3. Molecules with two independent centers

Now we will analyse the behaviour of a monolayer with two different species as a simple model similar to that of an adsorbed molecule with two independent redox centers. In order to do this, we have prepared a mixture of two antraquinones of similar structure: the sodium salts of the 9,10-antraquinone-2,6 disulfonic acid (AQDS) and of the 9,10-antraquinone-2 sulfonic acid (AQS). These quinones present two electron and two proton conversions in acidic media, with the protons transfer being non rate limiting and, therefore, they behave as reversible two electron processes [9].

By studying separately the LSV responses of each individual quinone, we have observed that they show a very similar peak height (i.e., a similar surface coverage), half peak width equal to 45 mV (i.e., corresponding to a simple charge transfer of two electrons), and the peak potentials of AQDS and AQS are separated around 30–40 mV (see insert curves in Fig. 6). Next, we analyzed the behaviour of a monolayer formed from an equimolar mixture of both AQDS and AQS moieties and, as in the previous cases, we checked the reversibility of the response from the superposition.
between the \((f'\nu)/\nu\) vs. \(E\) (solid lines) and \((dQ/dE)\) vs. \(E\) (white dots) responses for different scan rates (the curves in the figure correspond to \(\nu=0.7\, \text{V s}^{-1}\)). After that, by combining the values of the peak potential \((\Delta E^0)\) and \(\Delta E^0\) obtained using the working curve in Fig. 2b (dotted lines), we obtained: \(E^0_1 = 3\, \text{mV}\) and \(2\, \Delta E^0 = 62\, \text{mV}\) (i.e., \(K = 3.34\)). Finally, from Eq. (27), we obtained \(Q_m = 23\, \text{nC} (\Gamma = 2.3 \times 10^{-11}\, \text{mol cm}^{-2})\). With these values we calculated the theoretical \((dQ/dE) - E\) curve from Eq. (20) shown in this figure (black dots), which agrees perfectly with the experimental ones (note that we have changed \(F/RT\) by \(2F/RT\) in the expressions of \(J\) and \(K\) in this equation).

5. Conclusions

We have obtained expressions for the electrochemical response of dependent and independent multicenter redox molecules attached to the electrode surface with Differential Staircase Voltammetry (DSVC, \(dQ/dE\) vs. \(E\) curves) and Cyclic Voltammetry (LSV).

In DSVC, the potential perturbation employed has a discrete nature, such that the charge is usually sampled at times much greater than those involved in the non-desired double layer charging processes, thus allowing an effective de-coupling of the non-faradaic components of the response [32,34].

The use of both CV and DSCV has a great interest because the reversibility of the charge transfer processes can be proved from the coincidence of the Cyclic Voltammetric curves divided by the scan rate and the Differential Staircase Voltammetric curves.

The response of molecules with dependent and independent redox centers is logically coincident when \(\Delta E^0 = (E^0_2 - E^0_1) < 0\) (separate responses). Moreover, in the case of dependent centers, the \(\Delta E^0\) value permits the elicitation of the repulsive or attractive nature of the interactions existing between them [22]. The particular case of \(\Delta E^0 = -35.6\, \text{mV}\), corresponding to non interacting centers, gives rise to a DSVC or CV curve which has the same half peak width as that corresponding to a simple charge transfer but an intensity amplified by the number of redox centers in the molecule in a similar way to that observed for solution soluble bimolecular molecules [1–3].

Expressions have been obtained for the peak height and peak potentials of the DSVC or CV curves corresponding to dependent or independent centers, together with simple criteria for diagnosing each type of surface process, stepwise or independent. The theoretical predictions have been verified with three different systems, obtaining in all the cases the surface coverages and the formal potentials of the electroactive centers.

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