Analytical Solutions for the Study of Multielectron Transfer Processes by Staircase, Cyclic, and Differential Voltammetries at Disc Microelectrodes

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ABSTRACT: Key processes in (bio)electrochemistry involve multiple electron transfers. The study of the stability of the different oxidation states and the interaction between redox centers is fundamental to understand these processes. In this paper, simple analytical equations are presented for multielectron transfer processes in cyclic voltammetry (CV) and staircase cyclic voltammetry (SCV) at disc electrodes of any size. This provides a simple simulation method for the electrochemical response without demanding computing. The use of CV and SCV, and the corresponding differential techniques, for the characterization of these redox systems is analyzed. Procedures and criteria are given for transient and stationary conditions. The theoretical results are applied to the experimental study of the reduction of anthraquinone-2-sulfonate in water on gold macro- and microdisc electrodes.

1. INTRODUCTION
Multielectron transfers are widespread in the electrochemistry of nanoparticles,1 organic and organometallic compounds,2–5 as well as key biomolecules such as DNA6–7 and neurotransmitters.8 The characterization of these events includes the determination of the thermodynamic stability of the different oxidation states and, in the case of multicenter molecules, the interactions between redox centers with the subsequent inference of structural information. Electrochemical methods are very valuable for the study of these systems, and much effort is devoted to the development of the relevant theory and analysis procedures.9–19

In this paper, we contribute to the field by deriving analytical expressions for the study of reversible multielectron transfer processes at disc microelectrodes via cyclic voltammetry (CV), staircase cyclic voltammetry (SCV), and the corresponding differential techniques. CV is the most widely used electrochemical technique, being very suitable for quick, qualitative analyses. However, the real perturbation applied by modern instrumentation corresponds to SCV, which additionally enables further reduction of background current by adjusting the value of the sampling time. Microelectrodes are commonly used for studying biological systems for which miniaturization of electrochemical devices is essential. Small electrodes also offer other significant advantages derived from reduced ohmic drop and capacitative effects. Among microelectrodes, the disc shape is the most widely used due to its easier fabrication and cleaning.

The analytical expressions obtained in this paper are valid whatever the size of the electrode and the difference between the formal potentials of the successive electron transfers. Further, they enable any electrochemist to perform the simulation of electrochemical experiments readily without demanding programming. Curves and procedures for the extraction of the formal potential of the different steps are given for the EE mechanism at disc and (hemi)spherical microelectrodes.

When the peaks of cyclic (staircase) voltammograms are poorly defined, due to sigmoidal or overlapping waves, the use of differential techniques is recommended.20 Differential staircase (DSCV) and differential cyclic (DCV) voltammetries simply require differentiation of the signal obtained in SCV and CV, respectively. As a result, peaks better resolved are obtained which allow for the characterization of the system from their height and position.

The theoretical results are applied to the experimental study of the two-electron reduction of anthraquinone-2-sulfonate (AQ) in water on gold electrodes:

\[
\begin{align*}
\text{AQ} + e^- & \rightleftharpoons \text{AQ}^+ + E_1^0 \\
\text{AQ}^{2+} + e^- & \rightleftharpoons \text{AQ}^2- + E_2^0
\end{align*}
\]

As an anthraquinone derivative, this compound is particularly interesting for the catalytic reduction of oxygen which is of biological and industrial importance.21–24

The stability of the different species is remarkably affected by the coexisting ions in solution with the corresponding shift of...
the formal potentials of the electron transfers.\textsuperscript{25} Accordingly, the difference between the formal potentials can be tuned through the composition of the background electrolyte. This behavior is studied in this paper on gold macro- and microdisc electrodes.

2. EXPERIMENTAL SECTION

2.1. Chemical Reagents. Anthraquinone-2-sulfonic acid sodium salt monohydrate (AQ, Sigma-Aldrich, 97%), tetramethylammonium hydroxide pentahydrate (TMAOH, Sigma-Aldrich, >97%), tetra-n-butylammonium hydroxide 30-hydrate (TBAOH, Sigma-Aldrich, >99%), ferrocene (Fe(C_{6}H_{5})_{2}, Aldrich, 98%), acetonitrile (MeCN, Fischer Scientific, dried and distilled, 99%), and tetra-n-butylammonium perchlorate (TBAP, Fluka, Puriss electrochemical grade, 99%) were all used as received without further purification.

2.2. Instrumentation. A computer-controlled \( \mu \)-Autolab potentiostat type II (Eco-Chemie, Netherlands) was employed to undertake the electrochemical experiments. A three-electrode setup was employed with a platinum wire as the counter electrode and a saturated calomel electrode (SCE, Radiometer, Denmark) as the reference electrode. As working electrode, gold disc electrodes were employed with radii \( r_{D} = 14 \) \( \mu \)m and \( r_{0} = 0.9 \) \( \mu \)m. Prior to experiments the working electrodes were polished on alumina lapping compounds (BDH) of decreasing size (1–0.3 \( \mu \)m) and sonicated in ultrasound bath for 3 min. The solutions of AQ were bubbled with nitrogen before each experiment, and positive pressure of \( \text{N}_{2} \) was maintained throughout.

The calibration of the gold microelectrode was carried out electrochemically from the steady-state limiting current of the oxidation of a 2 mM solution of ferrocene in acetonitrile containing 0.1 M TBAP:\textsuperscript{26}

\[
I_{0}^{0} = 4r_{D}FDc^{0} \tag{2}
\]

A value of the diffusion coefficient of ferrocene in MeCN of \( D = 2.43 \times 10^{-9} \) m\(^{2}\) s\(^{-1}\) at 25 °C was adopted.\textsuperscript{27}

3. THEORY

Let us consider the reduction of a solution soluble molecule with \( n + 1 \) possible oxidation states \( O_{1}, O_{2},..., O_{n+1} \)

\[
O_{1} + e^{-} \rightleftharpoons O_{2} E_{1}^{0'}
\]

\[
O_{2} + e^{-} \rightleftharpoons O_{3} E_{2}^{0'}
\]

\[
\vdots
\]

\[
O_{n} + e^{-} \rightleftharpoons O_{n+1} E_{n}^{0'} \tag{3}
\]

where \( E_{i}^{0'} \) (\( i = 1, 2, n \)) are the formal potentials of each electron transfer. The incidence of comproportionation reactions on the voltammetric response can be discarded if the diffusion is the only mass transport mechanism, the value of the diffusion coefficient is the same for all the species \( O_{i} \), the electron transfers are reversible, and any other chemical reaction is absent.\textsuperscript{11,14,28}

By following the procedure detailed in the Appendix, the following expression for the current at the \( p \)th potential pulse is obtained

\[
I{(p)} = FAD \sum_{m=1}^{p} \frac{1}{\sqrt{2\pi \Delta t}} \exp \left( -\frac{(n-i+1)j_{i}(E_{m})}{\sqrt{2\pi \Delta t}} \right) \tag{4}
\]

where the time function \( g(t_{eq}) \) is dependent on the electrode size and shape

\[
g_{p}(t) = \frac{1}{\sqrt{\pi \Delta t}} \text{ planar electrode} \tag{5}
\]

\[
g_{p}^{s}(t) = \frac{1}{\sqrt{\pi \Delta t}} + \frac{1}{r} \text{ spherical electrode} \tag{6}
\]

\[
g_{d}(t, r_{D}) = \frac{4}{\pi r_{D}} \left[ 0.7854 + 0.44315 \frac{r_{d}}{\sqrt{\Delta t}} + 0.21446 \exp \left( -0.39115 \frac{r_{d}}{\sqrt{\Delta t}} \right) \right] \text{ disc electrode} \tag{7}
\]

with \( r_{d} \) and \( r_{D} \) being the radius of the spherical and disc electrodes, respectively. Note that function \( g(t) \) for the case of disc electrodes is obtained from the semiempirical Shoup and Szabo equation.\textsuperscript{29} In a previous paper\textsuperscript{30} it was found by comparison with numerical results that it gives rise to accuracy better than 0.5%.

The potential function \( f_{O}(E_{m}) \) (\( m = 1, 2, ..., p \) ) is independent of the electrode geometry

\[
f_{O}(E_{m}) = c_{0}^{(m-1)}(q_{\text{surface}}) - c_{0}^{(n)}(q_{\text{surface}}) \tag{8}
\]

where \( c_{0}^{(i)}(q_{\text{surface}}) \) is the surface concentration of species \( i \) at the \( m \)th pulse such that \( c_{0}^{(0)}(q_{\text{surface}}) = c_{0}^{*} \), \( c_{0}^{(n)}(q_{\text{surface}}) = 0 \), and for \( m \geq 1 \):

\[
c_{O}^{(m)}(q_{\text{surface}}) = \frac{c_{O}^{*}(1 + \sum_{i=1}^{n} (\prod_{j=m}^{n} j_{i}(E_{m})))}{1 + \sum_{i=1}^{n} (\prod_{j=m}^{n} j_{i}(E_{m}))} \tag{9}
\]

3.1. Staircase and Cyclic Voltammetries. Next, eq 4 will be particularized for the electrochemical techniques staircase cyclic voltammetry (SCV) and cyclic voltammetry (CV).\textsuperscript{31} Thus, we consider the application of successive potential steps with the same pulse length, \( \Delta t \), and a pulse amplitude \( \Delta E \). This potential-time program corresponds to SCV, and it is the real perturbation applied by digital instruments.\textsuperscript{32,33} When the \( \Delta E \) value is very small (\( \Delta E < 0.01 \) mV\textsuperscript{34}), the potential waveform behaves as a ramp (i.e., a continuous function of time) such that the response in SCV coincides with that in CV where

\[
E(t) = E_{\text{initial}} - vt \text{ for } t \leq \lambda \tag{10}
\]

\[
E(t) = E_{\text{final}} + vt \text{ for } t > \lambda
\]

with \( \lambda \) being the time at which the scan is reversed in cyclic voltammetry and \( v \) the scan rate defined as \( v = \Delta E/\Delta t \). The time elapsed between the beginning of the \( m \)th pulse and the end of the \( p \)th pulse will be given by

\[
(p - m + 1)\tau = \frac{|E_{p-m+1} - E_{\text{initial}}|}{v}, \quad m = 1, 2, ..., p \tag{11}
\]

Taking into account eq 4, the expressions for the SCV and CV currents of multielectron processes at disc, hemispherical, and planar electrodes of any size can be expressed as
\[ \Psi\phi = \frac{I\phi}{FACo_s \sqrt{D_{2v}}} = \sum_{m=1}^{p} g(\xi, \theta_{mp}) \sum_{i=1}^{n} (n - i + 1) f(O_m(E_m)) \] (12)

where

\[ \xi = \frac{2 RT \theta_{mp}}{\sigma (E_{p-m+1} - E_{initial})}, \quad m \equiv 1, 2, ..., p \] (13)

\[ \theta_{mp} = \frac{F}{RT}(E_{p-m+1} - E_{initial}), \quad m \equiv 1, 2, ..., p \] (14)

\[ \hat{g}_p(\xi, \theta_{mp}) = \frac{1}{\sqrt{\pi \theta_{mp}}} \] (15)

\[ \hat{g}(\xi, \theta_{mp}) = \xi + \frac{1}{\sqrt{\pi \theta_{mp}}} \] (16)

\[ \hat{g}(\xi, \theta_{mp}) = \frac{4}{\pi} \left[ 0.7854 + \frac{0.44315}{\xi \sqrt{\theta_{mp}}} + 0.2146 \exp \left( \frac{0.39115}{\xi \sqrt{\theta_{mp}}} \right) \right] \] (17)

3.1.1. EE Mechanism. In the common case of two electron transfer processes (i.e., EE mechanism)

\[ O_1 + e^- \rightleftharpoons O_2 \quad E_1^0 \] \[ O_2 + e^- \rightleftharpoons O_3 \quad E_2^0 \] (18)

the above expression can be simplified to

\[ \Psi\phi_{EE} = \sum_{m=1}^{p} \hat{g}(\xi, \theta_{mp}) \Omega_m \] (19)

where

\[ \Omega_1 = e^{\theta_{initial}} \left( \frac{e^{\theta_{0}} + 2Ke^{\theta_{initial}}}{(e^{\theta_{0}})^2 + e^{\theta_{0}} e^{\theta_{initial}} + K e^{2\theta_{initial}}} \right) \] (20)

\[ \Omega_{m \geq 2} = e^{\theta_{initial}} \left( \frac{e^{\theta_{0}} + 2Ke^{\theta_{initial}}}{(e^{\theta_{0}})^2 + e^{\theta_{0}} e^{\theta_{initial}} + K e^{2\theta_{initial}}} \right) \] (20)

\[ \theta_{initial} = \frac{F}{RT}(E_{initial} - E_1^0) \] (21)

\[ \theta_{p} = \theta_{lp} = \frac{F}{RT}(E_p - E_{initial}) \] (22)

\[ K = \exp \left( \frac{F}{RT}(E_2^0 - E_1^0) \right) \] (22)

with \( K \) being the disproportionation constant of \( O_2 \):

\[ 2O_2 \rightarrow O_1 + O_3 \quad K = \frac{k_1}{k_2} \] (23)

For spherical electrodes, considering eqs 16 and 20, the expression for the (S)CV current can be written as

\[ \Psi\phi_{EE,sphe} = \xi \theta_p + \frac{1}{\sqrt{\pi}} \sum_{m=1}^{p} \Omega_m = \xi \theta_p + \Psi\phi_{EE,planar} \] (24)

where

\[ \theta_p = e^{\theta_{initial}} \left( \frac{e^{\theta_{0}} + 2Ke^{\theta_{initial}}}{(e^{\theta_{0}})^2 + e^{\theta_{0}} e^{\theta_{initial}} + K e^{2\theta_{initial}}} \right) \] (25)

Similarly, the expression for disc electrodes becomes

\[ \Psi\phi_{EE,disc} = \xi \left( \theta_p + 0.2732 \sum_{m=1}^{p} \Omega_m \exp \left( -\frac{0.39115}{\xi \sqrt{\theta_{mp}}} \right) \right) + \Psi\phi_{EE,planar} \] (26)

4. RESULTS AND DISCUSSION

4.1. Staircase Cyclic Voltammetry (SCV) and Cyclic Voltammetry (CV). In Figure 1 the effects of the scan rate and electrode radius on cyclic voltammograms of different EE processes are analyzed through the dimensionless sphericity parameter, \( \xi \). Hereafter, we will consider that the current is sampled at the end of each potential pulse of the potential staircase; nevertheless, the analytical expressions are valid whatever the time selected to record the current.

According to its definition (eq 13), large values of parameter \( \xi \) are associated with small electrode radii and/or slow scan rates. Therefore, as \( \xi \) is increased, the dimensionless current \( (\Psi\phi) \) of the forward scan increases, whereas the backward peaks decrease due to diffusion of the electrogenerated species toward the bulk solution. Moreover, the shape of the forward voltammogram varies from peak to sigmoidal-shaped as the steady state is reached.

The influence of the electrode geometry on the voltammetry also depends on the scan rate and the electrode radius. For large electrodes and/or fast scan rates, the dimensionless voltammograms obtained at disc and (hemi)spherical electrodes coincide (with a difference in the peak current less than 5% for \( \xi < 0.3 \), see Figure 3). Under these conditions, the diffusion is almost linear such that the current density is the same as on macroelectrodes. On the other hand, the larger the \( \xi \) value (i.e., the smaller the electrode and/or the slower the scan rate), the more apparent the differences are between the responses at electrodes of different shapes. In such conditions, the diffusion domains at disc and (hemi)spherical electrodes differ significantly, the current density being greater at discs. In the limit of steady state conditions, the dimensionless currents for any value of the potential, at any (direct or differential) electrochemical technique, and whatever the number of electrochemical steps are related by the following: \( \Psi\phi_{disc}/\Psi\phi_{sphe} = 4/\pi \).

The variation of voltammograms at disc and (hemi)spherical microelectrodes \( (r_0 = 2\mu m) \) with the difference between the formal potentials, \( \Delta E^{\theta} = E_2^0 - E_1^0 \), shown in Figure 2.

The two waves turn into a single one as the \( \Delta E^{\theta} \) value becomes more positive for reduction processes. When two waves are obtained, the extraction of the \( \Delta E^{\theta} \) value is straightforward from the difference between the half-wave potentials \( (E_{1/2}^0, E_{2/2}^0) \) or from the difference \( E_{peak}^0 - E_{1/2}^{10.12} \).
When a single wave is recorded, the determination of \( \Delta E^\prime_0 \) is performed from the values of the current of the forward peak through the plots shown in Figure 3. These include the values predicted for disc and (hemis)spherical electrodes at different “sphericity” conditions (i.e., different \( \xi \) values), including the planar limit when \( \xi \to 0 \).

The study of the variation of the peak current with the scan rate is also of interest given that this is a very common method of characterization of redox systems and it can give rise to significant errors when used inappropriately. The following relationships are obtained for the forward peak current of the EE mechanism as a function of the parameter \( \xi = ((D/r_0^2)(RT/Fv))^{1/2} \) at disc electrodes (with an error less than 1% in the value of the peak current for \( 0.2 < \xi < 1 \))

\[
\psi_{\text{EE, disc peak}} = 1.047 + 2.138\xi \quad \Delta E_0^0 > 200 \text{ mV}
\]
\[
\psi_{\text{EE, disc peak}} = 0.981 + 2.174\xi \quad \Delta E_0^0 = 100 \text{ mV}
\]
\[
\psi_{\text{EE, disc peak}} = 0.793 + 2.206\xi \quad \Delta E_0^0 = 0 \text{ mV}
\]
\[
\psi_{\text{EE, disc peak}} = 0.744 + 2.161\xi \quad \Delta E_0^0 = -35.6 \text{ mV}
\]
\[
\psi_{\text{EE, disc peak}} = 0.699 + 2.194\xi \quad \Delta E_0^0 = -50 \text{ mV}
\]
\[
\psi_{\text{EE, disc peak}} = 0.644 + 2.226\xi \quad \Delta E_0^0 = -75 \text{ mV}
\]
\[
\psi_{\text{EE, disc peak}} = 0.602 + 2.265\xi \quad \Delta E_0^0 = -100 \text{ mV}
\]

and at (hemis)spherical electrodes

\[
\psi_{\text{EE, sphere peak}} = 1.174 + 1.733\xi \quad \Delta E_0^0 > 200 \text{ mV}
\]
\[
\psi_{\text{EE, sphere peak}} = 1.123 + 1.744\xi \quad \Delta E_0^0 = 100 \text{ mV}
\]
\[
\psi_{\text{EE, sphere peak}} = 0.928 + 1.752\xi \quad \Delta E_0^0 = 0 \text{ mV}
\]
\[
\psi_{\text{EE, sphere peak}} = 0.834 + 1.749\xi \quad \Delta E_0^0 = -35.6 \text{ mV}
\]
\[
\psi_{\text{EE, sphere peak}} = 0.787 + 1.775\xi \quad \Delta E_0^0 = -50 \text{ mV}
\]
\[
\psi_{\text{EE, sphere peak}} = 0.726 + 1.805\xi \quad \Delta E_0^0 = -75 \text{ mV}
\]
\[
\psi_{\text{EE, sphere peak}} = 0.682 + 1.833\xi \quad \Delta E_0^0 = -100 \text{ mV}
\]

4.2. Differential Staircase Cyclic Voltammetry (DSCV) and Differential Cyclic Voltammetry (DCV). As can be seen in Figures 1 and 2, the peaks in (staircase) cyclic voltammograms are not well-defined as they approach steady state conditions. In this situation, the use of differential staircase cyclic voltammetry (DSCV) and differential cyclic voltammetry (DCV) is more appropriate and accurate. In these techniques, the current corresponding to two successive points of the voltammogram are subtracted, \( \Delta I = I_{p+1} - I_p \), and the difference plotted versus the applied potential. The aim is to improve the shape and resolution of the peaks (see Figure 4).

Typically, the value of the potential corresponding to the first pulse, \( E_{p1} \), is chosen as the potential axis. However, the use of the average value, \( (E_{p1} + E_p)/2 \), facilitates the analysis of the experimental results as will be discussed below. In Figure 4, the variation of DSCV curves with \( \Delta E^\prime_0 \) is plotted for the EE mechanism at disc and (hemis)spherical electrodes (through the dimensionless parameter eq 13 on the CV voltammograms of an EE mechanism at disc (---) and hemispherical (- -) microelectrodes. Different \( \Delta E^0 = E_2^0 - E_1^0 \) values are considered: (A) \(-200 \text{ mV}\), (B) \(0 \text{ mV}\), and (C) \(+200 \text{ mV}\). |\( \Delta E_0^\prime | = 0.01 \text{ mV}.

Figure 1. Influence of the scan rate and electrode radius (through the dimensionless parameter eq 13 on the CV voltammograms of an EE mechanism at disc (---) and hemispherical (- -) microelectrodes. Different \( \Delta E^0 = E_2^0 - E_1^0 \) values are considered: (A) \(-200 \text{ mV}\), (B) \(0 \text{ mV}\), and (C) \(+200 \text{ mV}\). |\( \Delta E_0^\prime | = 0.01 \text{ mV}.
mechanism at disc microelectrodes. The informative parameters are the peak potentials when the peaks are separated, and the peak current and peak potential when a single wave is recorded. Note that the procedures discussed below are easier and more accurate than the analysis of sigmoidal, stationary (S)CV voltammograms.

In the case of two separate peaks, the difference between the peak potentials coincides with the difference between the formal potentials for $\Delta E^0_{0}' < -110$ mV. The value of the formal potentials can be extracted from the average value of the peak potentials of the forward and backward scans:

$$E^0_1' = \frac{E_{1,\text{peak}}^\text{forward} + E_{1,\text{peak}}^\text{backward}}{2}$$

$$E^0_2' = \frac{E_{2,\text{peak}}^\text{forward} + E_{2,\text{peak}}^\text{backward}}{2}$$

(29)

Under steady state conditions, the response in differential techniques is equivalent to that in differential double pulse voltammetry. Thus, when the peaks are well separated, the peak potentials and the formal potential coincide when the value $(E_{p+1} + E_p)/2$ is used as the potential axis:

$$E^0_1' = (E_{1,\text{peak}}^\text{forward})_{ss} = (E_{1,\text{peak}}^\text{backward})_{ss}$$

$$E^0_2' = (E_{2,\text{peak}}^\text{forward})_{ss} = (E_{2,\text{peak}}^\text{backward})_{ss}$$

(30)

When a single peak is obtained, the determination of the formal potentials is possible from the peak current and peak potential. As can be seen in Figure 4d–f, the average values of the forward and backward peak potentials correspond to the average value of the formal potentials:

$$\frac{E^0_1' + E^0_2'}{2} = \frac{E_{1,\text{peak}}^\text{forward} + E_{1,\text{peak}}^\text{backward}}{2}$$

(31)

Complementarily, the peak current is a function of the difference between the formal potentials ($\Delta E^0 = \Delta E^0_2' - \Delta E^0_1'$), and its variations for the forward scan are given in Figure 5.

As a compilation of the theoretical results presented in this paper, in Figure 6 the simulated response for the four-electron oxidation of bis(1,2-diferrocenylthiolen)nickel is shown in all the techniques studied under transient (Figure 6a,c) and stationary (Figure 6b,d) conditions. This complex has four oxidizable ferrocenyl groups and a nickel dithiolene center such that multiple anodic and cathodic processes are possible.$^3$ In
Figure 6, the four oxidation steps that the neutral species can undergo are considered. As can be observed, the first two steps are well resolved whereas the third and fourth ones give rise to overlapped voltammograms.

Three different values for the pulse amplitude ($\Delta E$) are considered. Whereas no significant effect of the $\Delta E$ value on $\Psi$ is observed under steady state conditions, important differences are found in transient voltammograms. This serves as an alert about the treatment of experimental data obtained with digital instruments, which apply a staircase program that can be simulated rigorously and easily with the analytical expressions presented in this paper.

4.3. Experimental Results. The theory presented above has been applied to the experimental study of the two-electron reduction of anthraquinone-2-sulfonate (AQ) (see eq 1) in aqueous solution at gold disc electrodes. Tetramethylammonium hydroxide (TMAOH) and tetra-n-butylammonium hydroxide (TBAOH) in different proportions were used as supporting electrolyte. Hence, high pH was assured to ensure that the system follows a simple EE mechanism without coupled protonation reactions.

It has been reported that the tuning of the formal potentials of this redox system is possible by varying the electrolyte composition. The semiquinone intermediate is stabilized by ion pairing with the tetra-n-butylammonium cation, and consequently, the difference between the formal potentials of the electron transfers increases. This effect enables the study of a range of $\Delta E_0$ values by simply changing the proportion of TBAOH in solution. By combining both differential and direct techniques, we have studied the behavior of the formal potential of the electron transfers from transient and stationary voltammograms.

Figure 7 shows the results obtained at a gold macroelectrode ($r_0 = 0.9$ mm) with a scan rate $\nu = 100$ mV s$^{-1}$ such that transient, peak-shaped voltammograms are obtained. The potential–time program applied corresponds to staircase cyclic voltammetry with a pulse amplitude $\Delta E = 1.06$ mV. From the best fit of the experimental data with the analytical expressions here presented (eq 12), the values of the formal potentials of the two electron processes were extracted (see Table 1).

By increasing the proportion of TBAOH in solution, the voltammograms range from a single peak to two separated ones. Thus, the formal potential of the first electron transfer shifts toward less negative values whereas the opposite behavior is found for the formal potential of the second step. Both
results are consistent with the thermodynamic stabilization of the semiquinone intermediate (AQ$^{−}$) by ion pairing with the tetra-n-butylammonium cation.

The voltammograms obtained at a gold disc microelectrode ($r_0 = 14 \mu$m) with a scan rate $v = 20$ mV s$^{-1}$ are shown in Figure 8a. From the steady-state limiting current, the value of the diffusion coefficients of the electroactive species can be determined (see Tables 1 and 2).

In such conditions, the use of differential techniques is preferable. In Figure 8b the differential voltammograms are plotted, resulting from the subtraction of consecutive current points and smoothing by bisquare weighting and second-order polynomial regression. From the differential peaks, the value of

![Figure 6. Theoretical voltammograms in staircase cyclic voltammetry (A and B) and differential staircase voltammetry (C and D) at disc electrodes for the four-electron oxidation of bis(1,2-diferrocenyldithiolen)nickel in [NBu$_4$][PF$_6$]/CH$_2$Cl$_2$ solution ($E_2^0 - E_1^0 = 120$ mV, $E_3^0 - E_1^0 = 230$ mV, $E_4^0 - E_1^0 = 290$ mV$^3$). Electrode radius: $r_0 = 1$ mm (A and C), and $r_0 = 5 \mu$m (B and D); $v = 100$ mV s$^{-1}$, $|\Delta E|$ values indicated on the graphs.](image)

![Figure 7. Experimental blank-subtracted (—) and best-fit theoretical (points) voltammograms of 0.5 mM AQ/H$_2$O solutions supported with [TMAOH] + [TBAOH] = 0.1 M on a gold disc macroelectrode of 0.9 mm radius. The proportion [TBAOH]/[TMAOH] is indicated on the graph. $v = 100$ mV s$^{-1}$, $|\Delta E|$ = 1.06 mV, $T = 298$ K.](image)

<table>
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<tr>
<th>Electrolyte ($I = 0.1$ M)</th>
<th>100% TBAOH</th>
<th>(60 + 40)% TBAOH + TMAOH</th>
<th>100% TMAOH</th>
</tr>
</thead>
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<tr>
<td>$\Delta E^{10}$ ($E_2^0 - E_1^0$/mV)</td>
<td>-135</td>
<td>-100</td>
<td>-20</td>
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<td>$E_1^0$/mV$^{25}$</td>
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<td>-564</td>
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<td>$D \times 10^6$/cm$^2$ s$^{-1}$</td>
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<td>3.5</td>
<td>5.3</td>
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</tbody>
</table>

$^a$Versus SCE. $^b$Values obtained from the steady state limiting current.$^{25}$
the formal potentials is extracted from the peak potentials and peak current as described above. The values obtained are included in Table 2. In all cases, the \( E^0 \) values give rise to satisfactory agreement of experimental and theoretical voltammograms, and they compare well with those reported in the literature. \(^{25,38}\)

5. CONCLUSIONS

Analytical expressions have been derived for cyclic staircase voltammetry (CSV) and cyclic voltammetry (CV) of multi-electron, reversible transfer processes at disc microelectrodes. These are valid for any electrode size, any difference between the formal potentials, and they are easily computable.

Under transient conditions, the characterization of multi-electron transfer processes can be performed through the analysis of the peak currents and peak potentials of the (staircase) cyclic voltammograms. The corresponding working curves have been obtained for the case of the EE mechanism at disc and (hemisphere) spherical microelectrodes. The evolution of the peak current of cyclic voltammograms with the scan rate has also been studied, and analytical expressions for the adequate study of two-electron processes have been given.

Under steady state conditions, or when the waves of the different steps are not well-defined, the use of differential techniques is recommended. These techniques offer better defined, peak shaped responses, the height and position of which allow for the determination of the formal potentials of the successive electron transfers.

The theory has been applied to the study of the double reduction of anthraquinone-2-sulfonate in aqueous solution at gold disc macro- and microelectrodes. The effect of the composition of electrolyte solution on the formal potentials of corresponding boundary value problem for the concentration geometry is given by

\[
\begin{align*}
\frac{\partial c_i}{\partial t} &= D \left( \frac{\partial^2 c_i}{\partial x^2} + \frac{2}{r} \frac{\partial c_i}{\partial r} + \frac{\partial^2 c_i}{\partial z^2} \right) \quad \text{(disc electrode)} \\
\frac{\partial c_i}{\partial t} &= D \left( \frac{\partial^2 c_i}{\partial x^2} + \frac{2}{r} \frac{\partial c_i}{\partial r} + \frac{\partial^2 c_i}{\partial z^2} \right) \quad \text{(spherical electrode)} \\
\frac{\partial c_i}{\partial t} &= D \left( \frac{\partial^2 c_i}{\partial x^2} + \frac{2}{r} \frac{\partial c_i}{\partial r} + \frac{\partial^2 c_i}{\partial z^2} \right) \quad \text{(planar electrode)}
\end{align*}
\]

with \( D \) being the diffusion coefficient of species \( O_i \). The corresponding boundary value problem for the concentration profiles is given by

\[
\begin{align*}
t_1 &= 0, \quad q \geq q_{surface} \\
t_1 &= 0, \quad q \to \infty \quad \left\{ \begin{array}{l} c_{1,1}^{(1)} = c_{1,2}^{(1)} = 0 \\
q_{1,1}^{(1)} = q_{1,2}^{(1)} = 0 \end{array} \right. \\
t_1 &= 0, \quad q = q_{surface} \quad \sum_{i=1}^{n+1} \left( \frac{\partial c_i^{(1)}}{\partial q} \right)_{q=q_{surface}} = 0
\end{align*}
\]

When a potential pulse \( E_t \) is applied to the electrode, mass transport by diffusion for eq 3 is described by Fick’s second law

\[
\frac{\partial c_i}{\partial t} = -D \left( \frac{\partial c_i}{\partial x} \right) \quad \text{(plane electrode)}
\]

where \( c_{i,1}^{(1)} \) are the concentration profiles of species \( O_i \) and \( \hat{\delta}_{O_i} \) is the diffusion operator which depends on the electrode geometry.

\[
\hat{\delta} = \frac{\partial}{\partial t} - D \left( \frac{\partial^2 c_i}{\partial x^2} + \frac{2}{r} \frac{\partial c_i}{\partial r} + \frac{\partial^2 c_i}{\partial z^2} \right)
\]

The Appendix provides detailed information on the analytical derivations and further discussion on the application of these techniques.
where

\[ I_{i}^{(1)} = \exp \left( \frac{F(E_i - E_0)}{RT} \right) \]  

(A8)

c_{0}^* is the bulk concentration of the multielectron reducible molecule, and \( q \) the coordinate normal to the electrode surface: \( x \) for planar, \( r \) for (hemi)spherical, and \( z \) for disc electrodes.

Taking into account the assumption that the oxidation state does not affect the diffusivity of the molecules, it is demonstrated that the total concentration is conserved at any time and point of the solution independently of the reversibility of the electrode reactions and the electrode geometry:39

\[ \sum_{i=1}^{n+1} c_{i}^{(1)} = c_{0}^* \]  

(A9)

Combining this expression with the Nernstian relationships between surface concentrations (eq A7), one finds that the surface concentrations of all the species are constant and given by

\[ c_{i}^{(1)}(q_{\text{surface}}) = \frac{c_{i}^{*} \prod_{m=1}^{n+1} I_{m}^{(1)}}{1 + \sum_{m=1}^{n+1} \left( \prod_{m=1}^{n+1} I_{m}^{(1)} \right)} \]  

(A10)

Hence, the problem of \( n + 1 \) electroactive species is simplified to \( n + 1 \) independent problems with constant limit and surface conditions. Therefore, the form of the solution for the surface flux of electroactive species is equivalent to that of diffusion limited chronoamperometry

\[ \left( \frac{\partial \tilde{c}_{i}^{(1)}}{\partial q} \right)_{q=0} = f_{i}(E_{i}) \times g(t_{i}); \ i \equiv 1, 2, ..., n + 1 \]  

(A11)

where the potential function is independent of the electrode geometry and is given by

\[ f_{i}(E_{i}) = c_{0}^* (q_{\text{surface}}) - c_{i}^{(1)}(q_{\text{surface}}) \]  

f_{i,2} = -c_{i,2}^{(1)}(q_{\text{surface}}) 

(A12)

The expression for the function \( g(t) \) depends on time and the shape and size of the electrode, and it is given by eqs 5–7.

The current obtained is the sum of the partial currents of the \( n \) steps

\[ I_{n}^{(1)} = \sum_{i=1}^{n} I_{i}^{(1)} \]  

(A13)

where

\[ \frac{I_{i}^{(1)}}{I_{n}^{(1)}} = \left( \frac{\partial c_{i}^{(1)}}{\partial q} \right)_{q=0} \]  

(A14)

Considering eq A11 we obtain the expression corresponding to the current of the \( i \)th electrochemical step

\[ \frac{I_{i}^{(1)}}{I_{n}^{(1)}} = \sum_{j=1}^{n} \left( \frac{\partial c_{j}^{(1)}}{\partial q} \right)_{q=0} g(t_{i}) \sum_{j=1}^{n} I_{j}(E_{j}) \]  

(A15)

and taking into account the expression for the surface flux given (eq A11), it is deduced that

\[ I_{i}^{(1)} = FADg(t_{i}) \sum_{j=1}^{n} \left( \sum_{j=1}^{n} I_{j}(E_{j}) \right) \]  

(A16)

Following a procedure analogous to that in ref 38, the solution for the problem corresponding to the application of \( p \) successive potential pulses, \( E_{1}, E_{2}, ..., E_{p} \) can be expressed as a linear combination of solutions

\[ c_{i}^{(p)} = c_{i}^{(1)} + \sum_{j=2}^{p} \tilde{c}_{i}^{(j)} \]  

(A17)

where \( \tilde{c}_{i}^{(j)} \) (\( j \equiv 2, 3, ..., p \)) are the solutions of the following differential equation problem

\[ \tilde{c}_{i}^{(p)}(E_{i}) = 0; \ i \equiv 1, 2, ..., n + 1 \]  

(A18)

\[ t_{p} = 0, \ q \geq q_{\text{surface}} \]  

(A19)

\[ t_{p} > 0, \ q \rightarrow \infty \]  

(A20)

where the surface concentrations in eq A20 are given by eqs 9. Analogously to the case of the first pulse, the surface flux of \( c_{i}^{(p)} \) (\( i \equiv 1, 2, ..., n + 1 \)) can be written as

\[ \left( \frac{\partial c_{i}^{(p)}}{\partial q} \right)_{q_{\text{surface}}} = f_{i}(E_{p}) \times g(t_{p}) \]  

(A21)

with

\[ f_{i}(E_{p}) = c_{i}^{(p)}(q_{\text{surface}}) - c_{i}^{(p-1)}(q_{\text{surface}}) \]  

(A22)

According to eq A17, the total surface flux of species \( O_{i} \) is given by

\[ \textbf{dx.doi.org/10.1021/jp302075t J. Phys. Chem. C 2012, 116, 11470--11479} \]
\[
\left( \frac{\partial \chi^{(p)}}{\partial q} \right)_{\text{kin}} = \sum_{m=1}^{p} f_{\chi}(E_m) \times g(t_{\text{app}})
\]

(A23)

where \(t_{\text{app}}\) is the time elapsed between \(t_p\) and the application of the \(n\)th pulse: \(t_{\text{app}} = \sum_{n}^{} t_n\).

From the definition of the total current (eq A13), finally we obtain the expression for the current at the \(p\)th potential pulse given by eq 4.

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