Charge–potential and capacitance–potential curves corresponding to reversible redox Langmuir submonolayers of quinizarine in aqueous acidic solutions

Angela Molina∗,1, Joaquín González
Departamento de Química Física, Facultad de Química, Universidad de Murcia, Espinardo, Murcia 30100, Spain
Received 3 June 2003; received in revised form 14 July 2003; accepted 18 July 2003

Abstract
This paper presents the experimental behavior of the interfacial charge–potential (Qs/E) and capacitance–potential (Cs/E) responses obtained for quinizarine (1,4-dihydroxyanthraquinone) monolayers on mercury in aqueous acidic solutions, by using chronopotentiometry and derivative chronopotentiometry with programmed (DCP) and constant currents (CC) and cyclic voltammetry (CV). The results obtained have been compared with previously obtained theoretical expressions for the Qs/E and Cs/E curves of reversible redox monolayers [J. Electroanal. Chem., 557 (2003) 157], in which non-faradaic effects have been taken into account. We have found a good agreement between theory and experimental data although the Qs/E and Cs/E curves obtained from chronopotentiometric techniques are more suitable than those corresponding to cyclic voltammetry. Accurate values of the surface redox potential, total excess, and capacitance (Cs) of quinizarine monolayers have been obtained.

© 2003 Elsevier Ltd. All rights reserved.

Keywords: Redox monolayers; Quinizarine; Reversible processes; Derivative chronopotentiometry; Cyclic voltammetry

1. Introduction
In this paper, we will analyze the experimental behavior of the charge–potential responses (Qs/E curves with Qs being the total interfacial charge and E the potential applied or measured), and of the capacitance–potential responses (Cs/E curves, with Cs being the total interfacial capacitance), obtained for the quinizarine (1,4-dihydroxyanthraquinone) system, in aqueous acidic solutions. Quinonoid monolayers and films immobilized on electrodes, such as quinizarine on mercury, have been investigated previously by numerous authors [1–6]. This system presents strong adsorption and a redox behavior which can be considered as reversible [1,7].

We have compared the experimental results obtained with the theoretical expressions deduced in a previous paper [8], in which the Qs/E and Cs/E curves of reversible redox monolayers are shown to be independent of the electrochemical technique from which they have been obtained. This is true even in the more complex case in which non-faradaic effects are taken into account [8,9]. Hence, the use of the Qs/E and Cs/E curves is of great interest in discriminating between electroactive monolayers of different redox reversibility as also in their characterization.

We have compared the experimental Qs/E and Cs/E curves obtained from chronopotentiometry and derivative chronopotentiometry with programmed (DCP) and constant currents (CC) of the form I(t) = I0eωt, I(t) = I0tu, and I(t) = I0 [7–15], and those obtained from cyclic voltammetry (CV) (I versus E curve), with theoretical predictions taking into consideration the presence of non-faradaic effects on the responses. The experimental results obtained show a good agreement with the theoretical predictions. However, these results also show that the Qs/E and Cs/E curves obtained from chronopotentiometric data are more suitable than those obtained from voltammetric ones. This is in line with experimental results previously obtained by various authors [16–19], who point out that derivative chronopotentiometry with constant current (DCC) allows a more efficient baseline correction, which gives much better sensitivity than that obtained in linear sweep voltammetry. Moreover, these authors observed a greater influence of...
non-faradaic effects and ohmic drop on the voltammetric curves (I versus E) than on the chronopotentiometric ones (dI/dE versus E) [16,17]. By combining the $Q/E$ and $C/E$ representations, it is very easy to obtain values of the total excess adsorbed, of the surface standard potential and of the non-faradaic capacitance of the monolayer. Given all the above, the use of the $Q/E$ and $C/E$ curves is highly useful in characterizing the behavior of electroactive monolayers.

2. Experimental

2.1. Apparatus

The computer driven potentiostat–galvanostat was designed and constructed by QUICELTRON (Spain). Pulse and waveform generation and data acquisition were performed using i-SBXDD4 and DAS16-330i (Computer Boards, USA) boards, respectively. All computer programs were written in our laboratory.

In the chronopotentiometric experiments, the current switch was performed when the potential attained a prefixed value (cathodic or anodic) at which we supposed that the transition time had already been reached. The necessary comparison was carried out by means of an interrupt service routine using the clock of the personal computer.

2.2. Electrodes

A three electrode cell was employed in the experiments. A static mercury drop electrode (SMDE) served as working electrode. The SMDE was constructed using a DME, EA 1019-1 (Metrohm), to which a home-made valve was sealed. 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 1.0 M electrode.

2.3. Signal processing

In the experimental chronopotentiometric and voltammetric measurements, we have used different digital noise filters of the instrument supported software. The experimental E versus t curves were smoothed by applying the moving average smoothing procedure proposed by Savitzky and Golay [20], and transformed to the corresponding charge–potential curves ($Q$ versus $E$ curves). The smoothed charge–potential curves obtained for the quinizarine system were numerically differentiated by using a finite differences formula of fifth degree [21] to obtain the capacitance–potential curves. The experimental voltammetric I versus E curves were also smoothed by applying the Savitzky and Golay procedure and then transformed into the corresponding charge–potential and capacitance–potential curves.

All the kinetic and thermodynamic values obtained for the quinizarine system correspond to series of five essays. The results obtained are the mean of the five experimental values. The errors correspond to the standard deviation.

2.4. Chemical reagents

HClO$_4$, ethanol (Merck, reagent grade), and quinizarine (Aldrich, reagent grade) were used as received. Quinizarine was dissolved in ethanol and then diluted with water until the final proportion of ethanol was 1% (quinizarine concentration was $10^{-3}$ M). All the solutions were freshly prepared. Quinizarine was adsorbed at the mercury surface at a potential $-0.40$ V for 30 s prior to measurements.

Water was bidistilled and nitrogen gas was passed through solutions for deaeration for 15 min prior to measurements.

3. Theory

In this paper, we consider the following surface electrode process taking place in a reversible redox monolayer,

$$\text{A}_{\text{adsorbed}} + \text{n}e^{-} \rightleftharpoons \text{B}_{\text{adsorbed}}$$

when the existence of an interfacial potential distribution according to the model proposed by Smith and White [22] is taken into account. We also assume for the adsorbate monolayer that the Langmuir isotherm is obeyed, that the adsorption coefficients of both electroactive species and the maximum surface coverage ($\Gamma^*$) are independent of the potential, and that the redox couple is not present in the solution, in such a way the following is fulfilled:

$$\Gamma_i = \Gamma_{i,0} + \Gamma_{i,0} \equiv \Gamma_{i}(t) + \Gamma_{i}(t)$$

with $\Gamma_i(t)$ and $\Gamma_i(0)$, $i = A$ or B, being the surface excesses of $i$ species corresponding to the beginning of the application of the perturbation to the electrode ($t = 0$) and to a time $t$, respectively.

Moreover, the surface charge transfer process given by Scheme (1) is reversible and the Nernst equation is fulfilled [11,23],

$$\phi^0 = \frac{\Gamma_{i}(t)}{\Gamma_{i,0} - \Gamma_{i}(t)}$$

with

$\phi = \frac{nF}{RT}(E - E^0) - (\phi_A - \phi_B)$

$E^0$ is the standard potential of the surface process for the Langmuir isotherm and $\phi_A$ and $\phi_B$ are the electrostatic potentials at the electron transfer plane and in the bulk solution, respectively. Moreover,

$$\phi^\text{ideal} = \frac{\Gamma_{i,0}}{\Gamma_{i,0}}$$
with \( \eta_{\text{initial}} \) being \((nF/RT)(E_{\text{initial}} - E^\circ - (\varphi - \varphi_0))\), and \( E_{\text{initial}} \) the potential when \( t \to 0 \). Eq. (4) points out that the initial potential fixes the initial values of the excesses of both electroactive species.

The non-faradaic capacitance of the redox monolayer, \( C_{\text{dl}} \), is given by \( C_{\text{dl}} = C_1(1 - \eta_0/\varepsilon_0) \), with \( C_1 \) being the constant capacitance of the monolayer, and can be considered as constant when the following requirements are fulfilled [22]:

\[
C_1/(F(1/(\varepsilon_0 nF A))/(\varepsilon_0 nF A))^1/2 < 1 \quad (5)
\]

with \( c_i \) being the molar concentration of the supporting electrolyte, \( \varepsilon_0 \) the permittivity of the free space, and \( \eta_0 \) being the dielectric constant of the solvent.

Under these conditions, the total interfacial charge-potential and capacitance-potential responses, \( Q(E) \) and \( C_s/E \) curves, respectively, are given by [8,9]

\[
Q_s(E) = nF \alpha_A \left\{ \frac{1 - \Omega e^\eta}{1 + \Omega e^\eta(1 + e^\eta)} \right\} (6)
\]

\[
C_s(E) = \pm \left( \frac{n^2F^2A_I}{RT} \frac{e^\eta}{1 + e^\eta} + C_1 \right) \frac{C_a(E)}{C_1} (7)
\]

with \( \eta = (nF/RT)(E - E^\circ) \). In Eq. (6), \( \Omega \) refers to the value of the ratio \( (I_{\text{anodic}}/I_{\text{cathodic}}) \) at the beginning of the application of the current or potential. Thus, when a cathodic current or potential is applied, \( \Omega_{\text{anodic}} < 1 \), whereas when an anodic current or potential is applied, \( \Omega_{\text{anodic}} > 1 \).

When the initial excess of the oxidized species is much greater than that of reduced species \( (I_{\text{anodic}} > I_{\text{cathodic}}) \), or when the initial excess of the reduced species is much greater than that of oxidized species \( (I_{\text{cathodic}} > I_{\text{anodic}}) \), then Eq. (6) is transformed into:

\[
Q_s(E)_{\text{cathodic}} = nF \alpha_A \left\{ \frac{1}{1 + e^\eta} + \frac{C_1 \eta}{n^2F^2A_I} \ln \Omega_{\text{cathodic}} + \eta \right\} \quad (8a)
\]

\[
Q_s(E)_{\text{anodic}} = nF \alpha_A \left\{ \frac{-e^\eta}{1 + e^\eta} + \frac{C_1 \eta}{n^2F^2A_I} \ln \Omega_{\text{anodic}} + \eta \right\} \quad (8b)
\]

The expression for the capacitance-potential curve is given by Eq. (7), independently of the value of \( \Omega \).

As has been demonstrated for reversible redox monolayers, the relationships between the total interfacial charge \( Q_s(E) \) and the potential (Eqs. (8a) and (8b)), and between the total interfacial capacitance \( C_s(E) \) and the potential (Eq. (7)), are independent of the electrochemical technique used to obtain them [8]. Hence, these equations are applicable to voltammetric and chronopotentiometric methods.

This, when chronopotentiometry with programmed current (CP) and derivative chronopotentiometry with programmed current (DCP) are used, the interfacial charge \( Q_s(E) \) and capacitance \( C_s(E) \) are given by:

- **Programmed current variable with a power of time**: \( I(t) = I_0 t^n \)

  Interfacial charge:

  \[
  Q_s = \int_0^t I_0 t^n dt = \left( \frac{I_0}{n+1} \right) (e^{\eta t} - 1) \quad (9a)
  \]

  Interfacial capacitance:

  \[
  C_s = \frac{dQ_s}{dE} = \left( \frac{I_0}{n+1} \right) \frac{de^{\eta t}}{dE} \quad (9b)
  \]

  - **Programmed current variable exponentially with time**: \( I(t) = I_0 e^{\alpha t} \)

  Interfacial charge:

  \[
  Q_s = \int_0^t I_0 e^{\alpha t} dt = \left( \frac{I_0}{\alpha} \right) (e^{\alpha t} - 1) \quad (10a)
  \]

  Interfacial capacitance:

  \[
  C_s = \frac{dQ_s}{dE} = \left( \frac{I_0}{\alpha} \right) \frac{de^{\alpha t}}{dE} \quad (10b)
  \]

  - **Interfacial charge variable exponentially with time**

  \[
  I(t) = I_0 e^{\alpha t} \]

  \[
  Q_s = \int_0^t I_0 e^{\alpha t} dt = \left( \frac{I_0}{\alpha} \right) (e^{\alpha t} - 1) \quad (10a)
  \]

  \[
  C_s = \frac{dQ_s}{dE} = \left( \frac{I_0}{\alpha} \right) \frac{de^{\alpha t}}{dE} \quad (10b)
  \]

Finally, when cyclic voltammetry is used, \( Q_s(E) \) and \( C_s(E) \) are given by:

- **Interfacial charge**: \( Q_s = \int_{E_i}^{E_f} I_{\text{CV}}(E) \frac{dE}{v} \quad (12a) \)

- **Interfacial capacitance**: \( C_s = \frac{1}{v} \frac{dE}{\int_{E_i}^{E_f} I_{\text{CV}}(E) \frac{dE}{v}} \quad (12b) \)

with \( I_{\text{CV}} \) being the current measured in this technique, and \( E_i \) and \( E_f \) the initial and variable applied potentials of the voltammetric sweeps.

According to Eqs. (9b), (10b), (11b) and (12b), the analysis of reversible redox monolayers with derivative chronopotentiometry (i.e., the \( (I_0/\alpha) (de^{\alpha t}/dE) \)) versus \( E \) curve when exponential currents are used; the \( (I_0/(n+1)) (de^{\eta t}/dE) \) versus \( E \) curve when power currents are used; and the \( I_0(dE/dt) \) versus \( E \) curve when constant currents are used.
must give analogous results to those obtained by means of cyclic voltammetry (i.e., to those obtained from the analysis of the \( I_CV/s \) versus \( E \) curve).

We must take into account that in the case of CV, the perturbation applied is a variable potential, and the charge and capacitance must be obtained from the current measured. However, in the case of CP, CC, DCP, and DCC, the charge and capacitance are calculated from the applied current and from the variation of the potential measured with a function of time, since the response obtained in this case is a variable potential.

According to Eqs. (6), (8a), and (8b), the theoretical \( Q_s/E \) curves present a distorted sigmoidal shape. In the case in which both electroactive species A and B are initially adsorbed, this curve presents an intercept point with the potential axis which corresponds to the adsorption cross potential, \( E_{ap} \), which is given by,

\[
E_{ap} = E^0 + \frac{RT}{nF} \ln \frac{\Gamma_{A0}}{\Gamma_{B0}}
\]

(13)

When both species are initially present and a cathodic current is applied, only the part of the \( Q_s/E \) response corresponding to \( Q_s > 0 \) is observed and, hence, Eq. (6) is only applicable for \( E > E_{ap} \) (i.e., \( \theta > 1/2 \)). For an anodic current, however, Eq. (6) is only applicable in these conditions for \( E < E_{ap} \) (i.e., \( \theta < 1/2 \)). When only one species is initially present, the \( Q_s/E \) curve does not present a cross potential.

The \( C_s/E \) curve given by Eq. (7) presents a peak whose potential is equal to the surface standard potential of the surface process \( (E_{peak} = E^0) \), and whose capacitance is \( (C_s)_{peak} = \pm (n^2 F^2 A \Gamma_i/(4RT) + C_1) \) [8,9].

In this work, we have focused our study on the behavior of reversible redox monolayers in order to verify experimentally the fulfilment of Eqs. (7), (8a) and (8b).

4. Experimental results and discussion: quinizarine in aqueous acidic media

We have studied the redox behavior of quinizarine (1,4-dihydroxyanthraquinone) in aqueous acidic solutions with chronopotentiometry and derivative chronopotentiometry with different programmed currents, chronopotentiometry and derivative chronopotentiometry with constant current, and also with cyclic voltammetry, in order to obtain the charge–potential and capacitance–potential responses of this system in these electrochemical techniques.

According to the literature, quinizarine is strongly adsorbed on mercury and behaves as reversible [1,7]. In all the experimental curves obtained, quinizarine was adsorbed at the mercury surface at a potential \(-0.40 \text{ V} \) for 30’s prior to measurements. This pre-treatment greatly improves the response of the formed redox monolayers.

4.1. Charge–potential response of quinizarine in aqueous acidic solutions

Firstly, we have studied the \( Q_s/E \) curves of quinizarine 10\( \mu \text{M/HClO}_4 \)/1.0 M system in an aqueous solution with 1% of ethanol, using chronopotentiometry with programmed currents of the form \( I(t) = I_0 e^{\theta t} \), chronopotentiometry with constant current, and cyclic voltammetry. We have compared the experimental results obtained with these techniques with the theoretical behavior of a reversible redox monolayer as described by Eqs. (8a) and (8b).

In the case of chronopotentiometry we have applied two consecutive programmed or constant currents of alternating sign and we have recorded the potential time curves. The cathodic and anodic charges \( Q_s \) have been calculated by integrating the applied currents, i.e., \( Q_s = \int_0^t (I(t))_{\text{applied}} dt \), and they have then been plotted versus the measured potential. In the case of CV, the cathodic and anodic charges are obtained by integrating the ratio between the measured currents and the voltammetric sweep rates, i.e., \( Q_s = \int_0^t (dE/v) \text{d}t \). The charge obtained thus is plotted versus the applied potential.

Fig. 1 shows the cathodic and anodic \( Q_s/E \) curves corresponding to quinizarine system for the application of CP with two consecutive programmed currents of alternating sign and we have recorded the potential time curves. The cathodic and anodic charges \( Q_s \) have been calculated by integrating the applied currents, i.e., \( Q_s = \int_0^t (I(t))_{\text{applied}} dt \), and they have then been plotted versus the measured potential. In the case of CV, the cathodic and anodic charges are obtained by integrating the ratio between the measured currents and the voltammetric sweep rates, i.e., \( Q_s = \int_0^t (dE/v) \text{d}t \). The charge obtained thus is plotted versus the applied potential.

We have compared the experimental results obtained with these techniques with the theoretical behavior of a reversible redox monolayer as described by Eqs. (8a) and (8b).

As can be observed in Fig. 1, the \( Q_s/E \) curves from CP, CC, and CV present a distorted sigmoidal shape, and do not present intercept points with the potential axis. This distorted shape clearly indicates that these curves are affected by non-faradaic effects. We assume that the reason for this distortion lies in the term \( (C_s/RT)/(\ln 2 + \eta) \), which appears in Eqs. (8a) and (8b) (see below). In spite of the non-faradaic influence on the charge–potential curves shown in this figure, they should be coincident, according to Eqs. (8a) and (8b), which predict that the \( Q_s/E \) curves are independent of the electrochemical technique used to obtain them. Furthermore, these curves should be independent of the type of programmed current applied, \( I(t) \), in the case of CP, and in that of the sweep rate value, \( v \), in CV.

From this figure it can be observed that both cathodic and anodic \( Q_s/E \) responses obtained from CP and CC are
practically superimposable, and do not depend on the values of the exponents \(u\) and \(\omega\) in the power and exponential currents, \(I(t) = I_0 u^t\) and \(I(t) = I_0 e^{\omega t}\), respectively, in the case of CP. However, the \(Q_s/E\) curves obtained from CV for two values of the sweep rate are not completely superimposable, their differences are especially noticeable at the cathodic and anodic potential zones of these curves. Moreover, the cathodic and anodic charges obtained from CV for a given potential are smaller than those corresponding to CP and CC, especially in the cathodic and anodic zones.

The non-faradaic influence on the \(Q_s/E\) curves can be easily evaluated by using Eqs. (8a) and (8b). Thus, we can re-write the expression for the charge–potential curve in the following way:

\[
Q_s(E) = Q_a(E) + Q_{dl}(E) \quad \text{(cathodic and anodic)}
\]

with

\[
(Q_a(E))_{\text{cathodic}} \approx \frac{nFA\Gamma_1}{1 + e^{\eta}} \quad (\Gamma_1 \approx \Gamma_{b,0})
\]

\[
(Q_a(E))_{\text{anodic}} \approx -\frac{nFA\Gamma_1}{1 + e^{\eta}} \quad (\Gamma_1 \approx \Gamma_{b,0})
\]

\[
(Q_{dl}(E))_{\text{cathodic}} = -C_1 \left( \frac{RT}{nF} \ln \Omega_{\text{cathodic}} - E' + E \right)
\]

\[
(Q_{dl}(E))_{\text{anodic}} = -C_1 \left( \frac{RT}{nF} \ln \Omega_{\text{anodic}} - E' + E \right)
\]

where \(\eta = (nF/RT)(E - E')\). \(Q_a(E)\) and \(Q_{dl}(E)\) are the adsorption and non-faradaic charges of the monolayer, respectively.

From Eq. (17) and (18) it is clear that, in these conditions, the non-faradaic contribution to the charge–potential curve, \(Q_{dl}(E)\), varies linearly with the electrode potential with a slope equal to \(C_1\). Thus, it is possible to obtain the experimental values of \(C_1\) by making a linear extrapolation of the...
anodic extreme of the cathodic $Q_s/E$ curve, since when $E \gg E^0$ ($e^\eta \gg 1$), it is fulfilled that $(Q_a)_{\text{cathodic}} \approx 0$, see Eqs. (14) and (15). In the case of the anodic $Q_s/E$ curve, this linear extrapolation must be made at the cathodic end, where $E \ll E^0$ ($e^\eta \ll 1$), and it is fulfilled that $(Q_a)_{\text{anodic}} \approx 0$, see Eqs. (14) and (16).

Fig. 2 shows the cathodic and anodic $Q_s/E$ curves corresponding to quinizarine 10$\mu$M/HClO$_4$ 1.0 M system in an aqueous solution with 1% of ethanol, for the application of CP with an exponential programmed current of the form $I(t) = I_0 e^{\omega t}$ ($\omega = 8 \text{s}^{-1}$), $I_0 = 1.5$ and $-1.5 \mu$A in both cathodic and anodic currents, respectively (solid lines). Total interfacial charge–potential curves ($Q_s/E$ curves); (dotted lines) non-faradaic charge–potential curves ($Q_{dl}/E$ curves); (dashed lines) adsorption charge–potential curves ($Q_a/E$ curves). Other conditions as in Fig. 1.

From the charge–potential curves shown in Fig. 1 it is also possible to obtain the surface standard potential of the redox couple, $E^0$. Thus, the sum of the interfacial cathodic
and anodic charges, is given by (see Eqs. (14)-(18)),

\[(Q_s/E)_{\text{cathodic}} + (Q_s/E)_{\text{anodic}} = nF \Delta \Phi \left[1 - e^{-}\frac{E}{\frac{RT}{F}}\right] + C_1 (E_{\text{initial}} + E_{\text{final}} - 2E)\]  

\[(19)\]

From Eq. (19) it can be easily deduced, by taking into account that in our experimental conditions only one species is present at the beginning of the cathodic and anodic charge-potential response, that:

\[(Q_s/E)_{\text{cathodic}} + (Q_s/E)_{\text{anodic}} = 0, \text{ for } E = E^0\]  

\[(20)\]

We should be aware that to make the sum shown in Eq. (19) it is necessary for the potential values to be the same in both cathodic and anodic \(Q_s/E\) curves. This can be done easily in the case of the charge-potential curves obtained from CV, due to the fact that in this technique the potential is the response obtained and is not controlled. In this case, the \(E^0\) value can be immediately obtained from the curves \((Q_s/E)_{\text{cathodic}} + (Q_s/E)_{\text{anodic}}\), if we take into account that when \(E = E^0\), it is fulfilled that \((Q_s/E)_{\text{cathodic}} = -(Q_s/E)_{\text{anodic}}\) (see Eq. (20)). Thus, in the case of the anodic and cathodic \(Q_s/E\) curves obtained from CV, the surface standard potential \(E^0\) can be easily determined as the intercept with the potential axis of the response obtained by adding both curves, as it is shown in Fig. 3a for the experimental charge-potential curves for the Quinizarine system obtained in CV for a sweep rate \(|v| = 4\text{ V s}^{-1}\). The \(Q_s/E\) curves are obtained from chronoamperometric data (CP and CC), it is better to obtain \(E^0\) as the potential corresponding to the intercept point of the \((Q_s/E)_{\text{cathodic}}/E\) and \(-(Q_s/E)_{\text{anodic}}/E\) curves, as it is shown in Fig. 3b which has been obtained from the experimental charge-potential curves for the quinizarine system corresponding to CP for the application of a programmed current of the form \(I(t) = Io\sin^2\), with \(u = 0.1\). In this figure we have also plotted the \(C_{iE}\) curves obtained for the quinizarine system in CV for two values of the sweep rate \(|v| = 4\text{ and 5 V s}^{-1}\) (white squares).

Table 1 shows the obtained values of \(E^0\) corresponding to the application of CP with two different programmed currents \((I(t) = Io\sin^2, I(t) = Io\sin^2\sin^2\), for the application of CC (\(I_0\)) and also those corresponding to the \(Q_s/E\) curves obtained for a sweep rate \(|v| = 4\text{ V s}^{-1}\).

4.2 Capacitance-potential response of quinizarine system

Now we will analyze the capacitance-potential responses of quinizarine system by using derivative chronopotentiometry with programmed currents (DCP), derivative chronopotentiometry with constant current (DCC), and cyclic voltammetry techniques.

In the case of DCP and DCC, the capacitance is directly calculated by differentiating the charge with respect to measured potential, i.e., \(C_s = \frac{dQ_s}{dE}\). Thus, for DCP with power time currents \(I(t) = Io\sin^2\), \(C_s\) is given by \((I_0/(u + 1) \frac{d\phi^2}{dE} + C_1\), for DCP with exponential currents of the form \(I(t) = Io\sin^2\), \(C_s\) is equal to \((I_0/(u + 1) \frac{d\phi^2}{dE}) + C_1\); and for DCC, \(C_s\) is given by \(I_0/(d\phi/dE)\). The capacitance thus obtained is plotted versus the measured potential. In the case of CV the capacitance \(C_s\) is directly obtained as the ratio between the current measured and the voltammetric sweep rate \(v\), and is plotted versus the applied potential.

Fig. 4 shows the \(C_{iE}\) curves corresponding to the quinizarine 10 μM HClO4 1.0 M system in an aqueous solution with 1% of ethanol, for the application of DCP with two programmed currents of alternating sign of the form \(I(t) = Io\sin^2\sin^2\) (solid lines), \(I(t) = Io\sin^2\) (a = 0.05 and 0.1, dashed lines); and for DCC (\(I_0\)) (black circles) to an SMDE, with \(I_0 = 1.5 \text{ and } 1.5\text{ μA}\) in both cathodic and anodic programmed and constant currents. In this figure we have also plotted the \(C_{iE}\) curves obtained for the quinizarine system in CV for two values of the sweep rate \(|v| = 4\text{ and 5 V s}^{-1}\) (white squares).

| Table 1 | Experimental total adsorption charge \((Q_s/E)\), total excess \((\Gamma_t)\), constant non-faradaic capacitance \((C_1)\) and surface standard potential \(E^0\) for the quinizarine 10 μM HClO4 1.0 M system in an aqueous solution with 1% of ethanol and on a SMDE, obtained from the charge-potential curves corresponding to CP, and CV shown in Fig. 1. \(I_0 = 0.031 \text{ cm}, \omega = 2 \text{ and } 296 \text{ K}\) |

<table>
<thead>
<tr>
<th>Chronopotentiometry with constant and programmed currents</th>
<th>Cathodic current</th>
<th>Anodic current</th>
<th>(E^0) (mV) vs. Ag/AgCl, KCl 1 M</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Q_{s,E}) (mC)</td>
<td>(I(t) \times 10^{12}) mol cm(^{-2})</td>
<td>(C_1) (μF cm(^{-2}))</td>
<td>(Q_{s,E}) (mC)</td>
</tr>
<tr>
<td>Exponential current (I(t) = Io\sin^2)</td>
<td>(a = 8\text{ s}^{-1})</td>
<td>92.9 ± 2.3</td>
<td>2.54 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>(a = 12\text{ s}^{-1})</td>
<td>99.7 ± 0.4</td>
<td>2.72 ± 0.02</td>
</tr>
<tr>
<td>Power time current (I(t) = Io\sin^2\sin^2)</td>
<td>(a = 0.05)</td>
<td>58.4 ± 0.3</td>
<td>2.50 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>(a = 0.10)</td>
<td>57.6 ± 0.4</td>
<td>2.47 ± 0.02</td>
</tr>
<tr>
<td>Constant current (I(t) = Io)</td>
<td></td>
<td>55.6 ± 0.4</td>
<td>2.38 ± 0.02</td>
</tr>
</tbody>
</table>

References:

- Table 1
- Fig. 4
- Eqs. (14)-(18), (19), (20)

Note: The text is a natural reading of the document, and the table has been reformatted for clarity.
The experimental values of the peak parameters (peak capacitance and potential, peak-to-peak splitting, ratio of cathodic and anodic peak capacitances and half-peak widths), of the curves shown in Fig. 4 appear in Table 2. The values obtained (an almost zero peak-to-peak splitting, and a ratio between cathodic and anodic peak capacitances equal to unity), are those expected for a reversible redox reaction with two electrons transferred in a monolayer with no lateral interactions between the adsorbates. However, the half-peak widths of both cathodic and anodic peaks are higher than those corresponding to the ideal case (45 mV) in the case of DCP and DCC of ~50 mV, and in the case of CV of ~55 mV.

In line with the theoretical results, the $C_p/E$ curves should be coincident, independently of the electrochemical technique employed to obtain them (see Eq. (7)). Moreover, in DCP and DCC these curves should be independent of the type of current (constant or programmed) applied, whereas in CV they should be independent of the sweep rate value, $v$. 

Fig. 3. (a) Experimental $(Q_s(E))_{cathodic}/E$, $(Q_s(E))_{anodic}/E$ and $(Q_s(E))_{cathodic} + (Q_s(E))_{anodic}/E$ curves for quinizarine 10 μM HClO$_4$ 1.0 M system in an aqueous solution with 1% ethanol on a SMDE corresponding to CV for a sweep rate $|v| = 4$ V s$^{-1}$. (b) Experimental $(Q_s(E))_{cathodic}/E$ and $-(Q_s(E))_{anodic}/E$ and curves for quinizarine 10 μM HClO$_4$ 1.0 M system in an aqueous solution with 1% ethanol on a SMDE corresponding to CP for a programmed current of the form $I(t) = I_0 u(t)$, $u = 0.1$. $I_0 = 1.5$ and $-1.5$ μA in both cathodic and anodic currents. Other conditions as in Fig. 1.
From this figure we can observe that the experimental \( C_s/E \) curves obtained from chronopotentiometric data (DCP and DCC), are practically independent of the type of current used (although in the case of DCC, the cathodic \( C_s/E \) curve presents slight differences in the peak region). However, the \( C_s/E \) curves obtained from voltammetric data cannot be considered as superimposable since they present different capacitance values in the peak and in the anodic potential region.

Following Eq. (7), from the peak potentials of curves in Fig. 4 we have obtained the \( E'_0 \) values shown in Table 2. These potential values are very similar and they are much less affected by the different electrochemical techniques employed to obtain them. The \( E'_0 \) values are in agreement with those previously obtained in the literature in analogous conditions [1,7].

When the constant non-faradaic capacitance condition is fulfilled, the double layer contribution to the experimental \( C_s/E \) curves has a constant value equal to \( C_1 \), independently of the electrochemical technique used. This value constitutes the so called “baseline” of the capacitance–potential curve \[11,22\]. Under these conditions, this curve should attain a constant value (\( \pm C_1 \)) at potentials quite far from the surface standard potential \( (E \ll E'_0 \text{ or } E \gg E'_0, \text{ see Eq. (7)}) \). The experimental results shown in this figure show that the capacitance–potential curves obtained from DCP and DCC take values which are practically constant in their cathodic and anodic limits, i.e., both DCP and DCC curves present a good and reproducible baseline. However, the \( C_s/E \) curves obtained from CV data (white squares), show that the capacitance does not reach constant values in their cathodic and anodic limits, and so the voltammetric \( C_s/E \) curves do not present good baselines. This fact has been previously reported by Wang [16], Kalvoda [17], Paleček and coworkers [18,19], in which the poor definition and high distortion observed in voltammetric peaks as compared to DCC ones under similar conditions are indicated. The values of \( C_1 \) obtained from the baselines of DCP, DCC, and CV curves in Fig. 4 are shown in Table 2. It can be observed that the capacitances \( C_1 \) corresponding to DCP and DCC are 10–25% smaller than that corresponding to CV, and present a smaller deviation.
Table 2: Experimental values for peak potentials, peak-to-peak splitting ($\Delta E_p$), ratio of cathodic and anodic peak capacitances ($R_c$), half-peak widths ($W_1$), surface standard potential ($E'_0$), total excess ($\Gamma_T$) and constant non-faradaic capacitance ($C_1$) for the Quinizarine $10\mu M$/$H_9262$ $M$/$HClO_4$ $1.0 M$ system in an aqueous solution with $1\%$ of ethanol obtained from the capacitance–potential curves corresponding to DCP, DCC, and CV shown in Fig. 4. $r_0 = 0.031$ cm, $n = 2$, $T = 298$ K.

<table>
<thead>
<tr>
<th></th>
<th>Cathodic current</th>
<th>Anodic current</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Delta E_p$ (mV)</td>
<td>$E_p$ (mV)</td>
</tr>
<tr>
<td>Exponential current</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$I(t) = I_0 e^{\omega t}$</td>
<td>$\omega = 8 s^{-1}$</td>
<td>1</td>
</tr>
<tr>
<td>Power time current</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$I(t) = I_0 u^a$</td>
<td>$\alpha = 0.05$</td>
<td>2</td>
</tr>
<tr>
<td>Constant current</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$I(t) = I_0$</td>
<td>$\alpha = 0.10$</td>
<td>1</td>
</tr>
<tr>
<td>Cyclic voltammetry</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$v = 4 V s^{-1}$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

For the cathodic sweep, $r_0 = 0.031$ cm, $n = 2$, $T = 298$ K.
Finally, we can easily obtain accurate values of the initial total excess $\Gamma_T$ from the capacitance–potential curves by subtracting from the capacitance peak the value of $C_1$, thus obtaining $|C_{\text{peak}} - C_1| \approx C_{\text{peak}} = n^2 F^2 A \Gamma_T / (4RT)$. By proceeding in this way with the $C/E$ curves shown in Fig. 4, we have obtained the experimental total excesses, $\Gamma_T$, shown in Table 2. From the results obtained we have observed that the total excess values measured from CV are 5% and 8–10% smaller than those corresponding to DCC and DCP, respectively, and present a slightly higher deviation. A similar fact has been previously reported by Forster [2], in which he obtained the total surface coverages of two anthraquinone derivatives on mercury (anthraquinone-2,6-disulfonic acid and anthraquinone-1,5-disulfonic acid), by using cyclic voltammetry and high speed chronoamperometry. In this reference, Forster reported that the surface coverages determined by cyclic voltammetry were 15% smaller than those obtained with chronocoulometry, but gave no reason for the possible origin of these differences.

In order to evaluate the agreement between experimental results obtained for the quinizarine system and theoretical predictions, we have plotted in Fig. 5 the experimental
cathodic \( Q_1/E \) (Fig. 5a) and \( C_1/E \) (Fig. 5b) curves for this system corresponding to the application of CV with a sweep rate \( |\omega| = 5 \text{Vs}^{-1} \) (white squares); to CP and DCP for the application of a programmed current of the form \( I(t) = I_0 \exp(\sigma t) \) (\( \sigma = 8 \text{s}^{-1} \), solid lines); and to CC and DCC with \( I_0 = 1.5 \mu\text{A} \) (black circles), together with the theoretical cathodic \( Q_1/E \) and \( C_1/E \) curves calculated using Eqs. (8a) and (7), respectively (white triangles). The theoretical curves have been calculated using the following parameters: \( C_1 = 100 \mu\text{Fcm}^{-2} \), \( T_1 = 2.38 \times 10^{-11} \text{molcm}^{-2} \) and \( E^0 = -0.178 \text{V} \).

In the case of the \( Q_1/E \) curves of Fig. 5a, we can see that there is a good agreement between experimental and theoretical results obtained from CP, CC, and CV in the anodic zone of these curves. However, in the cathodic region the experimental CV charges are smaller than the theoretical ones (see white squares), whereas the experimental CP and CC charges present good concordance with the theoretical curve.

The experimental results corresponding to the \( C_1/E \) curve obtained from DCP with exponential current present a good concordance with the theoretical curve (see Fig. 5b), whereas in that obtained from CV and DCC the agreement with the theory is not so good, with the widest discrepancies around the peak and in the anodic and cathodic limits.

To explain the discrepancies observed between the experimental results obtained in CV and the theoretical ones, it is of interest to take into account that, when deducing Eqs. (8a)-(8b) and (7) we have assumed that the non-faradaic capacitance has very little dependence on the electrode potential, i.e., \( C_0 \approx C_1 \). According to reference [22], this assumption is correct when Eq. (5) are fulfilled. In our experimental conditions the dimensionless parameters shown in these equations are equal to: \( I_0 \exp(\omega_1 T_{0c} R T_{0c})^{1/2} = 0.37 \) and \( C_1/(F 2.000 \exp(\omega_1 T_{c} R T_{c})^{1/2} = 0.044 \). According to our results, we can consider that the supposition of constant double layer capacitance is suitable for the \( Q_1/E \) and \( C_1/E \) curves obtained from chronopotentiometric data, and hence we can obtain accurate values of the thermodynamic parameters of the surface charge transfer by using Eqs. (7), (8a) and (8b). However, this assumption is not totally justified in CV and, therefore, the errors in obtaining thermodynamic parameters from Eqs. (7)-(8a) and (8b) are greater in this last technique.

## 5. Conclusions

We can conclude that the \( Q_1/E \) and \( C_1/E \) curves obtained from chronopotentiometric data are more in line with the theory than those obtained from voltammetric data. Concordance with theoretical predictions is higher and the experimental results are more reproducible when programmed currents are used (see Fig. 5 and Tables 1 and 2). Hence, chronopotentiometric techniques (CP, CC, DCP, and DCC) are more suitable than CV for the characterization of electroactive monolayers. Nevertheless, it is observed that, in general, experimental \( C_1/E \) curves are slightly broader than the theoretical ones, with the voltammetric \( C_1/E \) curves being those that differ most from theoretically predicted values. The reason for this behavior is not completely clear [22,24,25].

By combining the \( Q_1/E \) and \( C_1/E \) plots it is easy to obtain values of the total excess, of the surface standard potential as well as the non-faradaic capacitance of the monolayer. Given all the above, the use of the \( Q_1/E \) and \( C_1/E \) curves is of great interest in characterizing the behavior of electroactive monolayers.

## Acknowledgements

The authors greatly appreciate the financial support provided by the Dirección General de Investigación Científica y Técnica (Project no. BQI2000-0231) and by the Fundación SENECA (Expedient no. PB/53/FS/02).

## References