Study of an EE mechanism in additive differential pulse techniques

Angela Molina*, Marién M. Moreno, Manuela López-Tenés, Carmen Serna

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

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Abstract

Additive differential pulse techniques are applied to the study of a reversible EE mechanism. Analytical solutions are obtained in additive differential normal pulse voltammetry (ADNPV) and in additive differential pulse voltammetry (ADPV). The usefulness of these techniques in obtaining accurate simultaneous determinations of the formal potentials of both electrochemical steps when they are not completely separated is discussed and also applied to the study of the reduction of pyrazine in aqueous acid media. Excellent agreement between experimental results and theoretical predictions has been found. © 2002 Published by Elsevier Science B.V.

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1. Introduction

In a previous paper we obtained the rigorous analytical solutions for a reversible EE mechanism corresponding to any double potential step experiment, by analysing the response deduced in differential and reverse methods [1].

The aim of this paper is to apply the double pulse additive differential technique recently proposed, and described in [2], to the study of a reversible EE mechanism. This technique can be applied in normal mode when there is no restriction on the duration of either pulse, \( t_1 \) and \( t_2 \) additive differential normal pulse voltammetry (ADNPV), and by making the time of the first pulse much longer than that of the second, \( t_1 \gg t_2 \) additive differential pulse voltammetry (ADPV).

Independently of the value of the difference between the formal potentials of both electrochemical steps, \( \Delta E^0 \), the ADPV response presents a central zero-current point (central cross potential) which is given by \( (E_1^0 + E_2^0)/2 \) when the diffusion coefficients of species participating are equal and the number of electrons transferred in each step is also equal. This point exist whatever the species initially present in the solution and it represents a great advantage over other single and double pulse electrochemical techniques since it gives rise to an accurate simultaneous determination of \( E_1^0 \) and \( E_2^0 \) when both electrochemical steps are not completely separated.

In order to demonstrate the usefulness of these techniques, they have been applied to the study of the reduction of pyrazine in aqueous acid media [3–6]. The results obtained have lead to the determining of \( E_1^0 \) and \( E_2^0 \) for this system, and have shown the excellent agreement between the theoretical and experimental data.

2. Experimental

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 (ComputerBoards, USA) boards, respectively. All computer programs were written in our laboratory. The additive signal was obtained in a single experiment according to procedure described in [2].

A three electrode cell was employed in the experiments. A static mercury drop electrode (SMDE, electrode radius \( r_0 = 0.03 \) cm) 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.

For the SMDE, the errors due to the influence of the electrode sphericity in the measurement of the peak currents were less than 4% for \( t_2/t_1 \leq 0.05 \). In order to evaluate these errors we have compared Eq. (57) in [7] for a SMDE corresponding to the \( I^{\text{II}} \) vs. \( E \), with Eq. (58) in the same reference for the static plane electrode. The influence of the electrode sphericity on the peak potentials was negligible.

For the determination of peak values in additive techniques, we have used a second order polynomial fitting, taking the eight points nearest to the maximum or minimum. Cross potentials were obtained from a linear interpolation of the central zone of the curves.

Pyrazine, NaClO₄ and HClO₄ were of Merck reagent grade and were used without further purification. Water was bidistilled and nitrogen gas was used for deaeration. In all the experiments the temperature was kept constant at 25 ± 0.1 °C. In the theoretical calculations we have considered a value of \( D = 0.78 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1} \) for the diffusion coefficient of pyrazine [4].

### 3. Additive differential pulse techniques

The additive differential pulse techniques [2] are based on the obtention of the following two differential signals, corresponding to the same first pulse potential \( E^1 \) (see Scheme 1).

\[
\Delta I^c = I^{\text{Iic}}(E^{\text{Iic}}) - I^1(E^1),
\]

\[
\Delta I^a = I^{\text{IIa}}(E^{\text{IIa}}) - I^1(E^1)
\]

with \( |\Delta E| = -(E^{\text{Iic}} - E^1) = E^{\text{IIa}} - E^1 \) being \( \Delta E < 0 \) in Eq. (1) and \( \Delta E > 0 \) in Eq. (2).

In order to obtain the additive response, both differential signals \( \Delta I^c \) and \( \Delta I^a \) are added, such that

\[
I_{\text{ADNPV}} = \frac{(\Delta I^c + \Delta I^a) \sqrt{\pi \tau_2}}{FA \sqrt{D} c^*} = 2 \left( \frac{t_2}{t_1 + t_2} - \frac{t_2}{t_1} \right)
\]

\[
\times \left( X^1 - \frac{n_1^2 \gamma_{13} c_1^* - n_1 c_1^*}{c^*} \right) + (X^{\text{Iic}} - 2X^1 + X^{\text{IIa}})
\]

with

\[
X^1 = \frac{n_2 \gamma_{31} - n_1 J^1_{\text{Iic}}}{1 + \gamma_{23} J^1_{\text{Iic}} + \gamma_{13} J^1_{\text{IIa}}},
\]

\[
X^{\text{Iic}} = \frac{n_2 \gamma_{31} - n_1 J^{\text{Iic}}_1}{1 + \gamma_{23} J^{\text{Iic}}_1 + \gamma_{13} J^{\text{IIa}}_1},
\]

\[
X^{\text{IIa}} = \frac{n_2 \gamma_{31} - n_1 J^{\text{IIa}}_1}{1 + \gamma_{23} J^{\text{IIa}}_1 + \gamma_{13} J^{\text{IIa}}_1},
\]

\[
J^1 = \exp \left\{ \frac{n_F}{RT} (E^1 - E_0^1) \right\}
\]

\[
J^{\text{Iic}} = \exp \left\{ \frac{n_F}{RT} (E^{\text{Iic}} - E_0^{\text{Iic}}) \right\}
\]

\[
J^{\text{IIa}} = \exp \left\{ \frac{n_F}{RT} (E^{\text{IIa}} - E_0^{\text{IIa}}) \right\}
\]

\[
j = 1, 2.
\]

\[
c^* = \gamma_{13} c_1^* + \gamma_{23} c_2^* + c_3^*,
\]

\[
\gamma_{\text{mp}} = \sqrt{\frac{D_m}{D_p}},
\]

where \( D \) and \( c_i^* (i = 1, 2, 3) \) are, respectively, the diffusion coefficients and the initial concentrations of species \( O_1, O_2 \) and \( O_3 \), and \( A \) is the area of the electrode.
The expressions for the cathodic and anodic limit currents can be deduced from Eq. (4) by making $E^i, E^{\text{IIa}}$ and $E^{\text{III}} \to -\infty$ and $E^i, E^{\text{IIa}}$ and $E^{\text{III}} \to +\infty$, respectively. Thus, we obtain

$$I_{\text{ADNPV}}^{\text{lim}} = 2 \left( \frac{t_1}{t_1+t_2} - \frac{t_2}{t_1} \right) \left( \frac{n_1 c_1^2 + n_2 c_2^2}{c^*} \right).$$

(9)

$$I_{\text{ADNPV}}^{\text{lim}} = -2 \left( \frac{t_1}{t_1+t_2} - \frac{t_2}{t_1} \right) \left( \frac{n_1 c_1 c_2 + n_2 c_2}{c^*} \right).$$

(10)

From Eq. (4) can be easily demonstrated that in the case of $n_1 = n_2$ and $D_1 = D_2 = D_3$, the $I_{\text{ADNPV}}$ curves present a symmetry centre for any value of $\Delta E^0$, whose coordinates are given by

$$E_c = \frac{E^0_1 + E^0_2}{2},$$

(11)

$$I_c = 2 \left( \frac{t_1}{t_1+t_2} - \frac{t_2}{t_1} \right) \left( \frac{c_1^2 - c_2^2}{c^*} \right).$$

(12)

Fig. 1 shows the influence of the duration of the second potential step, $t_2$, on the theoretical ADNPV curves corresponding to a reversible EE process (Eq. (4)) for $n_1 = n_2, D_1 = D_2 = D_3$ and $\Delta E^0 = -200$ mV, obtained with $|\Delta E| = 40$ mV when only species $O_1$ is initially present in the solution. These curves, corresponding to well-separated steps, present four peaks whose heights are: $I_{M1}$ and $I_{m1}$ for the first step and $I_{M2}$ and $I_{m2}$ for the second one. According with Eqs. (9) and (10), the anodic limit current is always zero and the cathodic one is shifted towards more positive values when $t_2$ decreases and therefore, the current peaks ($I_{M1}$, $I_{m1}$, $I_{M2}$, $I_{m2}$) and the $I_c$ current are shifted in the same way (see Eq. (12)), whereas the $E_c$ potential is kept constant with $t_2$ (see Eq. (11)). In these conditions, this characteristic value $E_c$ can be easily calculate from these $I_{\text{ADNPV}}$ curves by

$$E_c = \frac{E^0_{M1} + E^0_{m2}}{2} = \frac{E^0_{M2} + E^0_{m1}}{2}.$$

(13)

When $t_2 \ll t_1$, the signal ADNPV converts to the ADPV one. So, by introducing this condition in Eq. (4) we have $I_{\text{ADPV}} = X^{\text{IIa}} - 2X^i + X^{\text{IIa}}$

(14)

with zero being the limit currents in this technique (see Eqs. (9) and (10)). Note that in contrast to the $I_{\text{ADNPV}}$ (Eq. (4)), the $I_{\text{ADPV}}$ (Eq. (14)) is independent of the species initially present in solution.

Figs. 2(a) and (b) show the theoretical ADPV curves for a reversible EE process (Eq. (14)) obtained with $|\Delta E| = 40$ mV and different values of the difference between the formal potentials of both electrochemical species initially present in solution. These curves present four steps, present four peaks whose heights are: $I_{M1}$ and $I_{m1}$ for the first step and $I_{M2}$ and $I_{m2}$ for the second one. According with Eqs. (9) and (10), the anodic and the cathodic peak currents are shifted towards more positive values when $t_2$ decreases and therefore, the current peaks ($I_{M1}$, $I_{m1}$, $I_{M2}$, $I_{m2}$) and the $I_c$ current are shifted in the same way (see Eq. (12)), whereas the $E_c$ potential is kept constant with $t_2$ (see Eq. (11)).

Fig. 1. Influence of $t_2$ on the ADNPV curves, $I_{\text{ADNPV}}/E^i$ for an EE mechanism when only species $O_1$ is initially present (Eq. (4)). $n_1 = n_2 = 1, D_1 = D_2 = D_3, T = 298.15$ K, $\Delta E^0 = -200$ mV, $|\Delta E| = 40$ mV, $t_1 = 2$ s. The values of $t_2$ (in s) are on the curves.

Fig. 2. Influence of $\Delta E^0$ on the ADPV curves, $I_{\text{ADPV}}/(E^i - E^{\text{IIa}})$, for an EE mechanism (Eq. (14)). $t_2 = 2$ s. The values of $\Delta E^0$ (in mV) are on the curves. The white circle corresponds to the point $(E_{0c}, 0)$. Other conditions as in Fig. 1.
zero current point (central cross potential) \( (E_{cc}, 0) \), where \( E_{cc} \) is given by Eq. (11).

When \( \Delta E^O \) \( \geq 200 \) mV the curves corresponding to an EE mechanism become indistinguishable from those corresponding to an E simple process with two electrons [2] (see corresponding curve in Fig. 2(a)).

Fig. 2(b) shows how, when \( \Delta E^O \) becomes more negative the two peaks separate out and four peaks begin to be clearly observed. Of these four, the two in the middle are of lower absolute value heights than the two end ones. If the \( \Delta E^O \) value continues to decrease, the absolute value of the four peaks evens out. In all the cases shown in this figure, three cross potentials are observed, of which the central, \( E_{cc} \) (Eq. (11)), is extremely useful in determining the formal potentials when the two steps of the EE mechanism are not well separated. Indeed, once the semism of the formal potentials is determined from the value of \( E_{cc}, E_1^O \) and \( E_2^O \) can be easily determined by adjusting the experimental ADPV curve to the theoretical one for the corresponding \( \Delta E^O \) value (see Fig. 3).

Note that in ADPV technique this central cross point exists whatever species is initially present in the solution. This represents a great advantage over other electrochemical techniques, be they single pulse (dc and NP voltammetries) or double pulse with \( t_2 \ll t_1 \) (RP and DP voltammetries), in which when only species \( O_1 \) (or \( O_2 \)) is initially present in the solution, no characteristic central cross point is observed, and which lead therefore to a far less accurate simultaneous determination of \( E_1^O \) and \( E_2^O \).

In order to demonstrate the usefulness of the additive techniques, Fig. 3 shows the experimental (dotted lines) and theoretical (solid lines) curves corresponding to the reduction of pyrazine in aqueous acid media, when this is the only species initially present in the solution, for different values of the pulse amplitude \( |\Delta E| \) and obtained with \( t_1 = 1 \) s and \( t_2 = 0.05 \) s. All the curves, as expected, are coincident at the symmetry centre, \( E_{cc} \), which in agreement with theoretical predictions is independent of \( |\Delta E| \). From this figure it can also be observed how only two peaks are obtained for high values of \( |\Delta E| \), but the typical behaviour of four peaks described above for an EE process is achieved by decreasing \( |\Delta E| \). These curves provide the value of \( E_c = -367 \pm 1 \) mV and the comparison between the experimental and theoretical curves has been made for a value of \( \Delta E^O = -117 \) mV, so we have obtained for \( E_1^O \) and \( E_2^O \) the values \( E_1^O = -308.5 \pm 1 \) mV and \( E_2^O = -425.5 \pm 1 \) mV. As can be seen, for these values the concordance between theoretical and experimental results is very good.

Finally, for \( \Delta E^O < -200 \) mV the ADPV curve corresponds to two well separated processes. In this situation the ADPV currents corresponding to the first and the second charge transfer reactions are given by

\[
I_{ADPV,1} = n_1 \gamma_{31} \left( \frac{1}{1 + \gamma_{21} \beta_{1c}} - \frac{2}{1 + \gamma_{21} \beta_{1c} + 1 + \gamma_{12} \beta_{1c}} \right)
\]

for the first charge reaction and

\[
I_{ADPV,2} = n_2 \gamma_{31} \left( \frac{1}{1 + \gamma_{22} \beta_{2c}} - \frac{2}{1 + \gamma_{22} \beta_{2c} + 1 + \gamma_{12} \beta_{2c}} \right)
\]

for the second. The two above expressions have been obtained from Eq. (14) by making \( J_2^o, J_{1c}^o, J_{2a}^o \rightarrow \infty \) and \( J_{1c}^o, J_1^o, J_{2a}^o \rightarrow 0 \), respectively.

In this case each of the separated ADPV curves has central symmetry with respect to its cross potential, \( E_{c,1} \) or \( E_{c,2} \), respectively, which are given by

\[
E_{c,1} = E_1^o - \frac{RT}{n_1 F} \ln \gamma_{12} = E_{rev,1}^{o/2},
\]

\[
E_{c,2} = E_2^o - \frac{RT}{n_2 F} \ln \gamma_{23} = E_{rev,2}^{o/2}.
\]

Note that when \( D_1 = D_2 = D_3 \) the difference between these last cross potentials coincides with the difference between the formal potentials of the EE mechanism, i.e.,

\[
E_{c,2} - E_{c,1} = \Delta E^O,
\]

whereas when both processes are not completely separated, as is the case of the experimental system shown in Fig. 3, this difference is always smaller than \( \Delta E^O \).

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