

## DIFFERENTIAL PULSE VOLTAMMETRY WITH A REVERSIBLE EE MECHANISM

M. M. Moreno, A. Molina\*, C. Serna, M. López-Tenés

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

### Abstract

An analytical equation corresponding to a reversible EE mechanism in differential pulse voltammetry is deduced. This technique is more suitable than d. c. voltammetry in order to distinguish an EE process from a single E mechanism when the formal potential values of both steps are close.

**Keywords:** Reversible EE mechanism, Differential pulse voltammetry.

### 1. Introduction

In spite of the interest of the study of electrode processes that occur with more than one step, until now only numerical solutions have been proposed for the analysis of an EE process in multistep potential techniques [1, 2].

In this work we deduce the analytical equation corresponding to the  $\Delta I/E$  response for an EE mechanism in the double pulse technique differential pulse voltammetry (DPV). To this end we have used the solutions previously deduced by us corresponding to a multistep process in d. c. voltammetry [3, 4].

The equation deduced here is valid for DPV technique when the two electrochemical steps are reversible and shows that the DPV technique is more suitable than d.c. voltammetry in order to distinguish an EE process from a simple E mechanism when the formal potential values of both steps are close. Furthermore, the DPV curve tends to separate out into two peaks as amplitude pulse,  $|\Delta E|$ , decreases. Thus, for example, when  $|\Delta E| = 50$  mV, two DPV curves appear when the difference between the formal potential of both steps is  $\Delta E^{0'} \leq -90$  mV, whereas when  $|\Delta E| = 30$  mV this separating appears for  $\Delta E^{0'} \leq -80$  mV.

When both steps give rise to two well separated DPV curves the expressions corresponding to their peak currents and peaks potentials can be easily deduced from the general equation given here.

2. Theory

The scheme of an EE mechanism is given by



where  $E_j^{0'}$  and  $n_j$  ( $j=1$  or  $2$ ) are, respectively, the formal potential and the number of electrons transferred in step  $j$ .

In our study of the preceding process we will suppose that both charge transfer reactions are reversible and that only species  $O_1$  is initially present in the solution with initial concentration  $c_1^*$ . If planar semi-infinite diffusion to and from the surface of the electrode takes place, then we have

$$\hat{\delta}_1 c_1(x,t) = \hat{\delta}_2 c_2(x,t) = \hat{\delta}_3 c_3(x,t) = 0 \quad (1)$$

with

$$\hat{\delta}_i = \frac{\partial}{\partial t} - D_i \frac{\partial^2}{\partial x^2} \quad (2)$$

The subindex  $i$  refers to the species  $O_i$  ( $i=1, 2$  or  $3$ ) considered in scheme (I), and  $D_i$  is the diffusion coefficient of species  $O_i$ .

The solutions of equations (1), i. e., the concentration profiles, obtained when a constant potential  $E^I$  is applied to the electrode during a time  $t_1$ , i. e.  $0 \leq t \leq t_1$ , (d. c. voltammetry with constant potential) are the following [3, 4]

$$\left. \begin{aligned} c_1^I(x,t) &= c_1^* + [c_1^I(0) - c_1^*] \operatorname{erfc} \left( \frac{x}{2\sqrt{D_1 t}} \right) \\ c_2^I(x,t) &= c_2^I(0) \operatorname{erfc} \left( \frac{x}{2\sqrt{D_2 t}} \right) \\ c_3^I(x,t) &= c_3^I(0) \operatorname{erfc} \left( \frac{x}{2\sqrt{D_3 t}} \right) \end{aligned} \right\} \quad (3)$$

We have introduced the superindex  $I$  and  $II$  in the notation in order to distinguish between the solutions corresponding to the application of potential  $E^I$  and those corresponding to that of potential  $E^{II}$  to the electrode (see below). In the above equation,  $c_1^I(0)$ ,  $c_2^I(0)$  and  $c_3^I(0)$  are the surface concentrations of species  $O_1$ ,  $O_2$  and  $O_3$  respectively, which are independent of time, and are given by the expressions [3, 4]

$$\left. \begin{aligned} c_1^I(0) &= \frac{J_1^I J_2^I \gamma_{13} c_1^*}{1 + \gamma_{23} J_2^I + \gamma_{13} J_1^I J_2^I} \\ c_2^I(0) &= \frac{c_1^I(0)}{J_1^I} \\ c_3^I(0) &= \frac{c_2^I(0)}{J_2^I} \end{aligned} \right\} \quad (4)$$

where

$$J_j^I = \exp \left\{ \frac{n_j F}{RT} (E^I - E_j^{0'}) \right\} \quad j = 1, 2 \quad (5)$$

$$\gamma_{pm} = \sqrt{\frac{D_p}{D_m}} \quad (6)$$

and the expression for the current at time  $t_1$  is the following [3, 4]

$$I^I(E^I, t_1) = FA \sqrt{\frac{D_1}{\pi t_1}} \{ (n_1 + n_2) [c_1^* - c_1^I(0)] - n_2 \gamma_{21} c_2^I(0) \} \quad (7)$$

If at time  $t_1$  the potential is stepped up to another constant value  $E''$ , which will be applied during a time  $t_2$  ( $0 \leq \tau_2 \leq t_2$ ), the boundary value problem corresponding to differential equation system (1) is, in these conditions

$$\tau_2 = 0, x \geq 0 : \quad c_i''(x, 0) = c_i'(x, t_1) \quad i = 1, 2, 3 \quad (8)$$

$$\tau_2 > 0, x \rightarrow \infty : \quad c_1''(x \rightarrow \infty, \tau_2) = c_1^*, \quad c_2''(x \rightarrow \infty, \tau_2) = c_3''(x \rightarrow \infty, \tau_2) = 0 \quad (9)$$

$\tau_2 > 0, x = 0:$

$$D_1 \left( \frac{\partial c_1''}{\partial x} \right)_{x=0} + D_2 \left( \frac{\partial c_2''}{\partial x} \right)_{x=0} + D_3 \left( \frac{\partial c_3''}{\partial x} \right)_{x=0} = 0 \quad (10)$$

$$\begin{aligned} c_1''(x=0) &= J_1'' c_2''(x=0) \\ c_2''(x=0) &= J_2'' c_3''(x=0) \end{aligned} \quad (11)$$

with

$$J_j'' = \exp \left\{ \frac{n_j F}{RT} (E'' - E_j^{o'}) \right\} \quad j = 1, 2 \quad (12)$$

As indicated above, the superindex  $II$  refers to the application of the second constant potential  $E''$ .

By following the dimensionless parameters method [5], in order to solve differential equations (1) with the boundary conditions (8)-(12), and supposing that  $t_1 \gg t_2$ , we deduce, for the current corresponding to this second potential step  $E''$ , the following expression

$$\begin{aligned} I''(E'', t_1 \gg t_2) &= FA \sqrt{\frac{D_1}{\pi}} \left[ \frac{1}{\sqrt{t_1}} \{ (n_1 + n_2) [c_1^* - c_1'(0)] - n_2 \gamma_{21} c_2'(0) \} + \right. \\ &\quad \left. + \frac{1}{\sqrt{t_2}} \{ (n_1 + n_2) [c_1'(0) - c_1''(0)] + n_2 \gamma_{21} [c_2'(0) - c_2''(0)] \} \right] \end{aligned} \quad (13)$$

In eq. (13),  $c_1'(0)$  and  $c_2'(0)$  are given by eqs. (4), and  $c_1''(0)$  and  $c_2''(0)$  are the concentrations of species  $O_1$  and  $O_2$  at the electrode surface ( $x=0$ ) during the application of the second potential step  $E''$ , and which have the form

$$\left. \begin{aligned} c_1''(0) &= \frac{J_1'' J_2'' \gamma_{13} c_1^*}{1 + \gamma_{23} J_2'' + \gamma_{13} J_1'' J_2''} \\ c_2''(0) &= \frac{c_1''(0)}{J_1''} \end{aligned} \right\} \quad (14)$$

In the DPV technique, the difference  $\Delta E = E'' - E'$  is kept constant and the response  $\Delta I = I'' - I'$  is recorded versus  $E'$  with the potential being scanned, for example, in the direction  $\Delta E < 0$ . This response can be obtained easily by subtracting equations (13) and (7). Thus, we deduce

$$\begin{aligned} \Delta I &= [I''(E'', t_1 \gg t_2) - I'(E', t_1)] \frac{\sqrt{\pi t_2}}{FA \sqrt{D_1}} = \\ &= (n_1 + n_2) [c_1'(0) - c_1''(0)] + n_2 \gamma_{21} [c_2'(0) - c_2''(0)] \end{aligned} \quad (15)$$

and taking into account the expressions for the surface concentrations,  $c_1'(0), c_2'(0), c_1''(0)$ , and  $c_2''(0)$  (eqs. (4) and (14)) we deduce

$$\Delta I = c_1^* \left\{ \frac{n_1 \gamma_{13} J_1' J_2' - n_2}{1 + \gamma_{23} J_2' + \gamma_{13} J_1' J_2'} - \frac{n_1 \gamma_{13} J_1'' J_2'' - n_2}{1 + \gamma_{23} J_2'' + \gamma_{13} J_1'' J_2''} \right\} \quad (16)$$

### 3. Results and discussion

In Fig. 1 we have represented the response obtained in DPV with  $|\Delta E| = 50$  mV for an EE mechanism with  $n_1 = n_2 = 1$  and different values of the difference between the formal potential of both electrochemical steps,  $\Delta E^{0'} = E_2^{0'} - E_1^{0'}$  (solid lines).

This figure shows that the two steps are perfectly detectable for very negative values of  $\Delta E^{0'}$  (in this example if  $\Delta E^{0'} \leq -90$  mV) due to the apparition of two peaks. For higher values of  $\Delta E^{0'}$ , only one peak is observed, which shifts to more positive potentials and whose peak current increases as  $\Delta E^{0'}$  becomes more positive.

We have also represented in Fig. 1 the DPV curve for a simple E process with two electrons ( $n = 2$ ) (dotted line) by selecting the value of formal potential,  $E^{0'}$ , equal to that corresponding to the first step of the EE mechanism,  $E_1^{0'}$ . Although in the case of a simple E process we obtain one peak at the same potential as in an EE mechanism with  $\Delta E^{0'} = 0$  (i. e.  $E_2^{0'} = E_1^{0'}$ ), the height of the peak is in this last case always smaller than that for an E process. From this figure it can also be deduced that the peak height of an EE mechanism is always lower than that corresponding to an E process if  $\Delta E^{0'} \leq 90$  mV. Therefore, in these conditions both processes are perfectly distinguishable in DPV, even when the EE mechanism only presents one peak.

The peak height value corresponding to an E process with two electrons is given by [6]

$$\Delta I_{peak}^{E \text{ process}} = 2c_1^* \tanh\left(\frac{F|\Delta E|}{2RT}\right) \quad (17)$$

and is reached in the case of an EE process when  $\Delta E^{0'} > 90$  mV. In these conditions, although the peak corresponding to an EE mechanism is shifted to more positive potentials in  $\Delta E^{0'}/2$  (i.e.  $E_{peak}^{EE} = E_{peak}^E + \Delta E^{0'}/2$ ), it will not be possible to distinguish both processes.

In Fig. 2 we show the  $I/E$  curve obtained in d. c. voltammetry for the same cases as considered in Fig. 1. As can be appreciated in this figure both curves, that

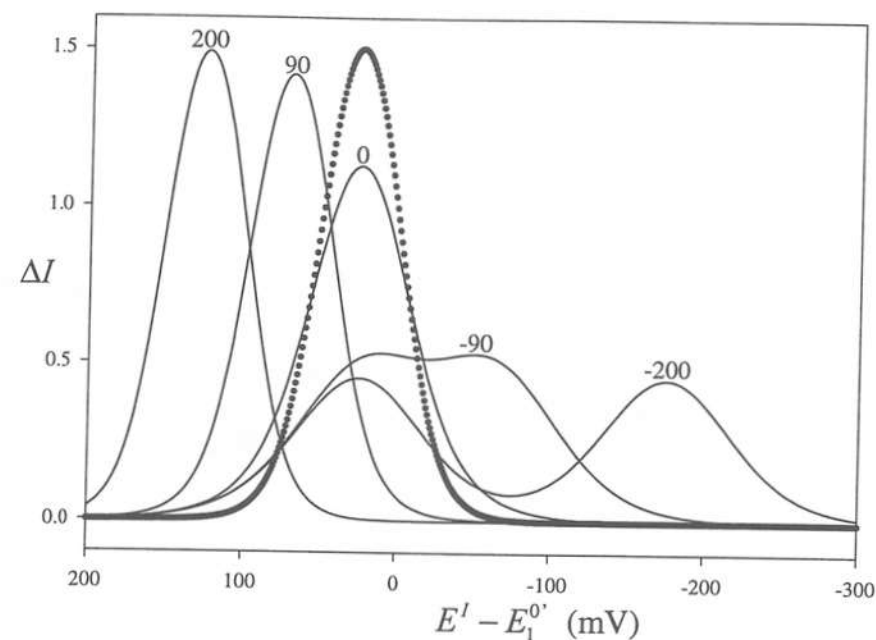


Fig. 1. Comparison of differential pulse voltammetry for a single step reaction with  $n=2$  (dotted line) and for a two step reaction (EE mechanism) with different  $\Delta E^{0'}$  (solid lines, eq. (16)).  $n_1 = n_2 = 1$ ,  $D_i = 10^{-5}$  cm<sup>2</sup>s<sup>-1</sup>,  $T = 298.15$  K,  $c_1^* = 1$  mM,  $|\Delta E| = 50$  mV. The values of  $\Delta E^{0'}$  (in mV) are on the curves

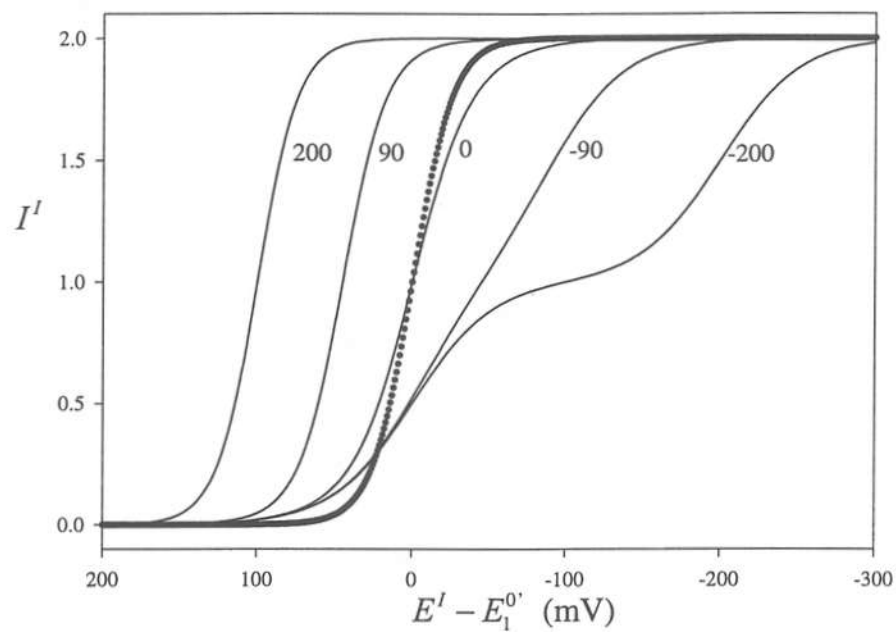


Fig. 2. Comparison of d. c. voltammetry for a single step reaction with  $n=2$  (dotted line) and for a two step reaction (EE mechanism) with different  $\Delta E^{0'}$  (solid lines, eq. (7)).  $n_1 = n_2 = 1$ ,  $D_i = 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ ,  $T = 298.15 \text{ K}$ ,  $c_i^* = 1 \text{ mM}$ ,  $|\Delta E| = 50 \text{ mV}$ . The values of  $\Delta E^{0'}$  (in mV) are on the curves.

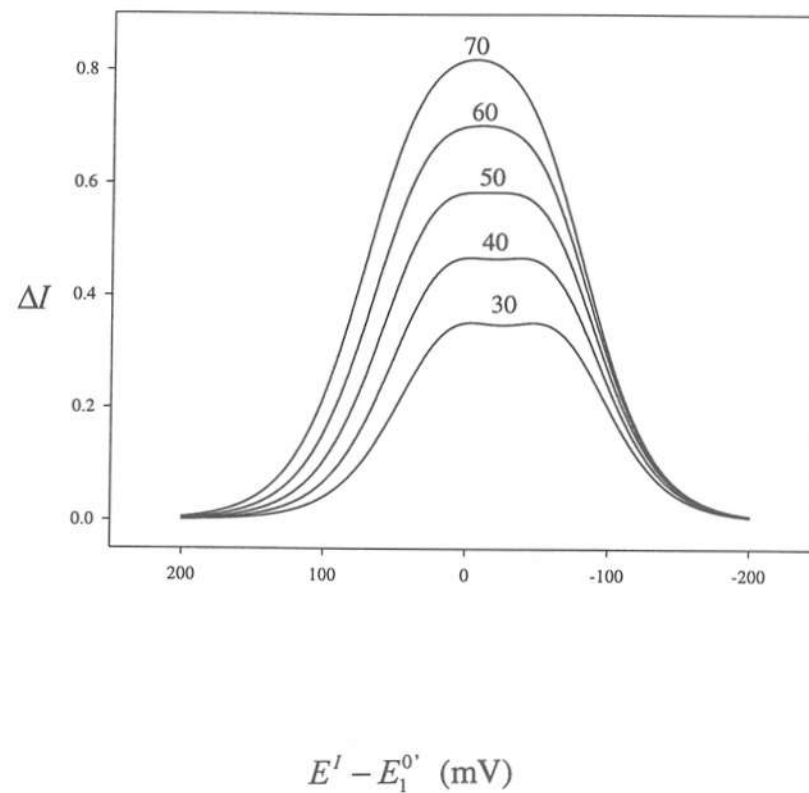


Fig. 3. Influence of pulse amplitude,  $|\Delta E|$ , on the differential pulse voltammograms for a two step reaction (EE mechanism) with  $\Delta E^{0'} = -80 \text{ mV}$ . The values of  $|\Delta E|$  (in mV) are on the curves. Other conditions as in Fig. 1.

corresponding to an EE mechanism and to an E process with two electrons, always present the same limit currents, and therefore both processes are difficult to distinguish in this technique when the EE mechanism presents only one wave ( $\Delta E^{0'} > -100$  mV). From the above, we can conclude that the DPV is more useful than d. c. voltammetry in order to distinguish an EE process from a simple E mechanism.

In Fig. 3 the influence of pulse amplitude,  $|\Delta E|$ , in DPV curves corresponding to an EE process with  $\Delta E^{0'} = -80$  mV is studied. As can be deduced from this figure, when the  $|\Delta E|$  value decreases the current decreases and the voltammogram tends to separate out into two peaks. Thus, by acting on the experimental conditions it is possible to detect at sight the existence of a two step process with DPV.

When  $E_2^{0'} \ll E_1^{0'} (E_2^{0'} - E_1^{0'} < -90$  mV) and  $|\Delta E| < 50$  mV the curves obtained in DPV present two well distinguished peaks (see Fig. 1). In this case (stable intermediate), the peak corresponding to the first charge transfer (whose formal potential is  $E_1^{0'}$ ) is that which appears at more positive applied potential values, for which it is verified that  $E^I$  and  $E^{II} \gg E_2^{0'}$  and therefore it is fulfilled  $J_2^I$  and  $J_2^{II} \rightarrow \infty$ . The other peak is due to the second step of the EE process and is located at applied potential values such that  $E^I$  and  $E^{II} \ll E_1^{0'}$  and thus  $J_1^I$  and  $J_1^{II} \rightarrow 0$

By introducing these assumptions in eq. (16) for  $\Delta I$ , two DPV curves are deduced whose expression are given by

$$\Delta I^{\text{first}} = n_1 c_1^* \left( \frac{1}{1 + \gamma_{12} J_1^{II}} - \frac{1}{1 + \gamma_{12} J_1^I} \right) \quad (18)$$

$$\Delta I^{\text{second}} = n_2 c_1^* \left( \frac{1}{1 + \gamma_{23} J_2^{II}} - \frac{1}{1 + \gamma_{23} J_2^I} \right) \quad (19)$$

From these equations it is possible to deduce the expressions for the potentials and currents of each of the peaks, giving

$$\left. \begin{aligned} E_{\text{peak}}^{I, \text{first}} &= E_1^{0'} - \frac{RT}{n_1 F} \ln \gamma_{12} + \frac{|\Delta E|}{2} \\ \Delta I_{\text{peak}}^{\text{first}} &= n_1 c_1^* \tanh \left( \frac{n_1 F |\Delta E|}{4RT} \right) \end{aligned} \right\} \quad (20)$$

$$\left. \begin{aligned} E_{\text{peak}}^{I, \text{second}} &= E_2^{0'} - \frac{RT}{n_2 F} \ln \gamma_{23} + \frac{|\Delta E|}{2} \\ \Delta I_{\text{peak}}^{\text{second}} &= n_2 c_1^* \tanh \left( \frac{n_2 F |\Delta E|}{4RT} \right) \end{aligned} \right\} \quad (21)$$

As is to be expected, these expressions are coincident with that obtained for two independent E processes with  $n_1$  and  $n_2$  electrons (see eq. (17)).

#### 4. Final comments

An analytical expression corresponding to the reversible EE mechanism in the double pulse technique DPV is deduced. This expression is applicable when the intermediate species is stable (EE consecutive process) as well as when the intermediate is unstable. In this last case, this technique is more suitable than the d. c. voltammetry for detecting the presence of a two step reaction.

#### Acknowledgements

The authors greatly appreciate the financial support provided by the Dirección General Científica y Técnica (Project No. BQU2000-0231), and by the Fundación Séneca (Project 00696/CV/99). Also M. M. M. thanks Fundación Séneca for the grant received.

#### References

- [1] Keh-Chang Tsaur, R. Pollard, *J. Electroanal. Chem.*, 183(1985)91.
- [2] I. Prieto, J. M. Pedrosa, M. T. Martín, L. Camacho, *J. Electroanal. Chem.*, 485(2000)7.
- [3] A. Molina, C. Serna, M. López-Tenés, R. Chicón, *Electrochem. Comm.*, 2(2000)267.

- [4] C. Serna, M. López-Tenés, J. González, A. Molina, *Electrochim. Acta*, EA 4376, in press.
- [5] J. Koutecky, *Czech. J. Phys.*, 2(1953)50.
- [6] D. Krulic, N. Fatouros, M. M. El Belamachi, *J. Electroanal. Chem.*, 385(1995)33.

## RECIPROCAL DERIVATIVE CHRONOPOTENTIOMETRY WITH EXPONENTIAL CURRENTS

J. Gonzalez and A. Molina\*

*Departamento de Química Física. Facultad de Química. Universidad de Murcia. Espinardo, 30100. Murcia, SPAIN.*

### Abstract

Theoretical expressions are presented which correspond to the response of adsorbed molecules which exhibit a reversible or totally irreversible charge transfer in Reciprocal Derivative Chronopotentiometry with constant current (RDC) and Reciprocal Derivative Chronopotentiometry with exponential current (RDCE).

In spite of the fact that RDC enjoys an important role in the elucidation of electrode processes, when this technique is applied to adsorbed molecules exhibiting an irreversible charge transfer, peaks are not observed. Under these conditions RDCE turns out to be more suitable than RDC. Furthermore, the use of programmed currents makes the selection of an appropriate range of transition times easier than does the use of constant currents.

Equations for the peak currents and peak potentials of the  $(dt/dE)/E$  and  $(de^{\omega t}/dE)/E$  curves for reversible and totally irreversible process are given in order to show the advantages of the use of the  $(de^{\omega t}/dE)/E$  curve when an exponential current time function is used.

**Keywords:** Reciprocal derivative chronopotentiometry, adsorption, programmed current, irreversible processes.

### Introduction

In the usual Reciprocal Derivative Chronopotentiometry with constant current (RDC) [1-12], the reciprocal derivative  $(dt/dE)$  of the  $E/t$  curve obtained when a constant current  $I_0$  is applied is represented versus the potential. In spite of the greater advantages of this technique, a serious disadvantage is observed when this technique is applied to adsorbed redox molecules exhibiting an irreversible behaviour since, in these conditions the reciprocal derivative chronopotentiograms do not present peaks.