

Additive differential pulse voltammetry, instead of double differential pulse voltammetry

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Abstract

A new electrochemical double pulse potential technique called additive differential pulse voltammetry (ADPV) is proposed. This technique is inspired by the original idea of Birke et al. [Anal. Chem. 53 (1981) 852] of recording two differential pulse (DP) voltammograms and it consists of plotting the sum of these two signals versus the first pulse potential, although in this paper the proposal is to obtain the ADPV signal through just one experiment. ADPV behaves in an identical way to the triple-pulse technique double differential pulse voltammetry (DDPV) for reversible processes when diffusion coefficients are equal for spherical electrodes and for any value of diffusion coefficients in planar electrodes. In the case of reversible electrode processes with amalgamation of reaction product or other more complex processes, ADPV is more advantageous than DDPV. This is due, among other reasons, to the fact that, under these conditions, a double potential step is much simpler to analyse than a triple potential step. © 2001 Published by Elsevier Science B.V.

Keywords: Additive differential pulse voltammetry; Double differential pulse voltammetry; Reversible process

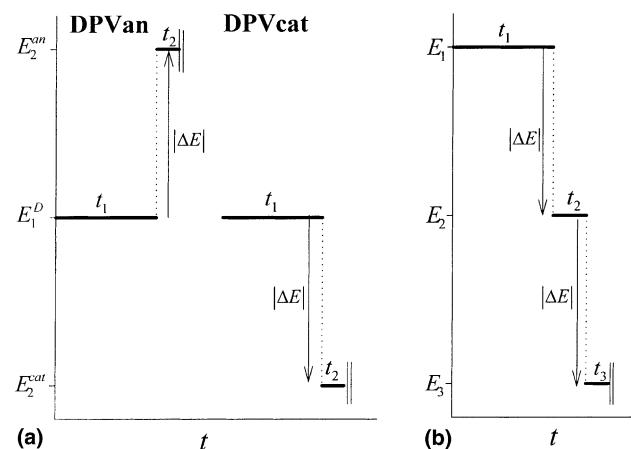
1. Introduction

Double and triple-pulse voltammetry techniques allow us to obtain electrochemical responses which are morphologically different depending on the electroodic reaction mechanism involved [1].

By using differential pulse (DP) polarographic technique, Birke et al. [2] established diagnostic criteria for different processes based on two DP recordings, one with cathodic, and the other with anodic, pulses of the same absolute value. If E_1^D is the first potential pulse in DP (where for the sake of convenience we introduce D superscript, see Scheme 1), the relation between the peak heights of the cathodic recording ($I_{DPV}^{cat} = I_2(E_2^{cat}) - I_1(E_1^D)$), where $E_2^{cat} = E_1^D - |\Delta E|$), and the anodic one ($I_{DPV}^{an} = I_2(E_2^{an}) - I_1(E_1^D)$), where $E_2^{an} = E_1^D + |\Delta E|$), enables us to distinguish between certain types of electroodic processes [2–7]. In Scheme 1(a) we show the potential–time waveform corresponding to anodic and

cathodic differential pulse voltammetry (DPV). In this scheme, t_1 and t_2 are the time of application for E_1 and E_2 potentials, respectively.

The double differential pulse voltammetry (DDPV) technique was proposed by us with the idea that the effects observed in the relation between the peak



Scheme 1. Potential–time wave form corresponding to: (a) ADPV technique, (b) DDPV technique.

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heights of the cathodic and anodic recording in DPV can be observed by using a triple-pulse of potentials [8,9].

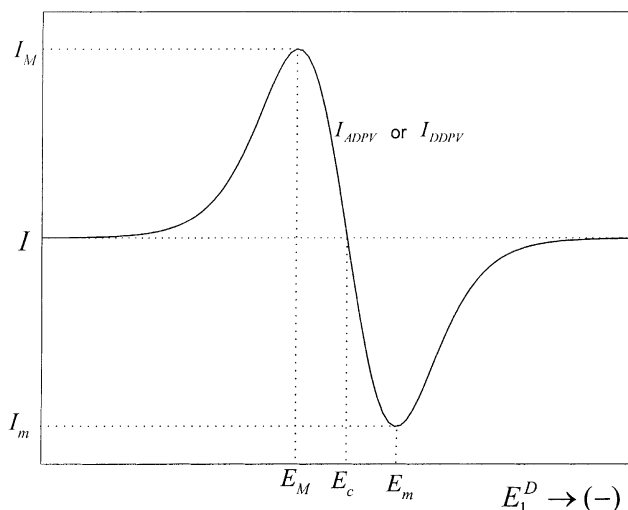
In the DDPV method we apply three successive potential steps E_1 , E_2 and E_3 , superimposed on a linear ramp, of durations t_1 , t_2 and $t_3 = 2t_2/3$, respectively (see Scheme 1(b)). The corresponding currents sampled at the end of each pulse will be I_1 , I_2 and I_3 , respectively. We shall also assume that $\Delta E = E_2 - E_1 = E_3 - E_2$ are constants and of the same sign. Under these experimental conditions, the current in DDPV has been defined as [8,9] $I_{\text{DDPV}} = I_3 - 2I_2 + I_1$ (see Scheme 2). This signal presents two peaks, one positive maximum (I_M) and one negative minimum (I_m) which appear for values of applied potentials E_M and E_m , respectively. The cross-potential value, at which $I_{\text{DDPV}} = 0$ is E_c . The DDPV technique is based on plotting I_{DDPV} versus E_1 or E_2 (in this work we have selected E_2 for the sake of convenience). Among the advantages of obtaining curves of this type, two stand out; the fact that E_c can be measured very accurately, and that the charge current is minimised to a large extent [9].

In this paper, we define a new technique consisting of adding the signals $I_{\text{DPV}}^{\text{cat}}$ and $I_{\text{DPV}}^{\text{an}}$, such that

$$I_{\text{ADPV}} = I_{\text{DPV}}^{\text{cat}} + I_{\text{DPV}}^{\text{an}} = I_2(E_2^{\text{cat}}) - 2I_1(E_1^{\text{D}}) + I_2(E_2^{\text{an}}).$$

This technique, based on plotting I_{ADPV} vs E_1^{D} , will be called additive differential pulse voltammetry (ADPV), and the $I_{\text{ADPV}}/E_1^{\text{D}}$ curve is obtained through just one double pulse experiment in the way described in Section 2. An example of the type of signal obtained using this technique is given in Scheme 2.

This paper demonstrates that the representations of I_{ADPV} and I_{DDPV} are morphologically similar. Moreover,



Scheme 2. I/E response for a reversible process in ADPV or DDPV.

these techniques are identical in the case of reversible processes with no amalgamation when both the electroactive species are initially present, and with equal diffusion coefficients in the case of spherical electrodes, and for any value of the diffusion coefficients in the case of planar electrodes.

When amalgamation occurs, the ADPV and DDPV techniques are not coincident, although they do, in certain aspects, present similar behaviours.

In this paper, we propose the introduction of the ADPV technique as a natural extension of double pulse techniques. This offers, among others, the following advantages:

1. Like the DDPV technique, ADPV presents curves in which E_c , the potential at which the signal is zero, can be measured with great accuracy. This parameter is closely related to the formal potential of the reversible processes.

2. In both ADPV and DDPV techniques, the charge current is minimised to a large extent with respect to traditional double pulse techniques such as DPV, or with respect to single pulse techniques, a feature which gives these techniques analytical advantages over those of DPV [9].

3. The ADPV technique is simpler to analyse than DDPV. Indeed, ADPV is a double pulse technique and, therefore, its mathematical treatment is much simpler than that corresponding to DDPV, for which it is necessary to obtain the response to a third potential pulse. This is especially important when amalgamation takes place and/or the diffusion coefficients are different [10–12], where the analytical solutions to the third potential pulse are highly complicated and difficult to manage. Thus, in these cases, if the aim is to take into account the higher-order spherical corrections (e.g., that of second-order), the solution to the problem when a double potential pulse is applied is quite complicated [13]. In the case of a third potential pulse, these corrections (which should be obtained for the DDPV technique) would be much more complicated, and, therefore, difficult to analyse, on account of the superposition principle's not being fulfilled. These complications can be removed by using the ADPV technique in which only two potential pulses participate.

4. The ADPV behaves as the double derivative voltammetry for small values of ΔE whereas the DDPV only presents this feature in the particular situation in which the ratio between the times corresponding to the third and second potential pulses is $2/3$.

5. The ADPV technique allows us to make diagnoses about the reaction mechanism based on the peak current measurements I_M and I_m (see Scheme 2) using solutions obtained previously in the literature on DPV. These are known for a large number of more complex electrode processes, both with and without kinetic complications [1].

2. Experimental

A three electrode cell was employed in the experiments. A static mercury drop electrode (SMDE, electrode radii $r_0 = 0.038$ and 0.026 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 electrodes were a Ag|AgCl|KCl 1.0 M electrode.

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 ADPV signal

$$I_{ADPV} = I_2(E_2^{\text{cat}}) - 2I_1(E_1^{\text{D}}) + I_2(E_2^{\text{an}})$$

was obtained in one experiment. To do this the following procedure was used. A potential at which no Faradaic reaction takes place is applied for 2 s in order to allow the drop to grow and the SMDE to stabilize (delay time). Then, potentials E_1^{D} and $E_1^{\text{D}} + |\Delta E|$ are applied over the time intervals t_1 and t_2 , respectively, and the current $I_1(E_1^{\text{D}})$ and $I_2(E_2^{\text{an}})$ are measured. Next, a new SMDE is used and after the delay time, the potential E_1^{D} and $E_1^{\text{D}} - |\Delta E|$ are applied over the same time intervals and the corresponding currents, $I_1(E_1^{\text{D}})$ and $I_2(E_2^{\text{cat}})$ are measured. Details about procedure and noise rejection were given in [14].

FeCl_3 , $\text{K}_2\text{C}_2\text{O}_4$ and $\text{H}_2\text{C}_2\text{O}_4$ were of Merck reagent grade. These chemical reagents were used without further purification.

Working solutions containing $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$ were freshly prepared in order to avoid possible oxidations of the anion oxalate by the Fe^{3+} . Water was bidistilled and nitrogen gas was used for deaeration.

In all the experiments the temperature was kept constant at $18 \pm 0.2^\circ\text{C}$.

3. Triple-pulse: double differential pulse voltammetry (DDPV)

The expression of I_{DDPV} has been defined as [8]

$$I_{DDPV} = I_3 - 2I_2 + I_1 \quad (1)$$

with $t_1 \gg (t_2 + t_3)$ and for any value of E_1 , E_2 , and E_3 . The currents I_1 , I_2 and I_3 for a reversible process have been obtained in [15] for spherical electrodes with the first spherical correction. When $t_3 = 2t_2/3$, Eq. (1) takes the form [15]

$$\begin{aligned} I_{DDPV}^N &= \frac{I_{DDPV} \sqrt{\pi t_3}}{nFA \sqrt{D_A c_A^*}} \\ &= \left\{ Z_3 - Z_2 + \frac{\sqrt{\pi D_A t_3}}{r_0} (Z_3 \Omega_3 - Z_2 \Omega_2) \right\} \left(1 + \frac{c_B^*}{\gamma c_A^*} \right) \\ &\quad + \frac{(\gamma \mp 1) \sqrt{D_A t_3}}{\gamma r_0} \left\{ \left(\frac{1 - K_1 c_B^*/c_A^*}{1 + \gamma K_1} \right) \right. \\ &\quad \times (Z_3 - Z_2) W \left(\frac{t_3}{t_1} \right) + Z_3 Z_2 \left(1 + \frac{c_B^*}{\gamma c_A^*} \right) W \left(\frac{2}{5} \right) \left. \right\}, \end{aligned} \quad (2)$$

where r_0 is the electrode radius.

$$\gamma = \sqrt{\frac{D_A}{D_B}} \quad (3)$$

and K_j , Z_j and Ω_j are given by

$$K_j = \exp \left\{ \frac{nF}{RT} (E_j - E^{0r}) \right\} \quad \text{with } j = 1, 2, 3, \quad (4)$$

$$Z_j = \frac{1}{1 + \gamma K_j} - \frac{1}{1 + \gamma K_{j-1}} \quad \text{with } j = 2, 3, \quad (5)$$

$$\Omega_j = \frac{1 \pm K_j}{1 + \gamma K_j} \quad \text{with } j = 1, 2, 3. \quad (6)$$

$W(x)$ is given by

$$W(x) = \frac{2}{\sqrt{\pi}} \left[\text{Arcsin}(\sqrt{x}) + \sqrt{x-1} \right]. \quad (7)$$

In the case in which $\Delta E = E_2 - E_1 = E_3 - E_2$, and if the pulses are applied in the negative direction ($\Delta E < 0$), it is fulfilled that (see Eq. (4))

$$\frac{K_2}{K_1} = \frac{K_3}{K_2} = e^{-\varepsilon} \quad (8)$$

with

$$\varepsilon = \frac{nF}{RT} |\Delta E|. \quad (9)$$

4. Double pulse: additive differential pulse voltammetry (ADPV)

The expression of I_{ADPV} is defined as

$$\begin{aligned} I_{ADPV} &= I_{DPV}^{\text{cat}} + I_{DPV}^{\text{an}} \\ &= I_2(E_2^{\text{cat}}) - 2I_1(E_1^{\text{D}}) + I_2(E_2^{\text{an}}). \end{aligned} \quad (10)$$

When $t_1 \gg t_2$, and taking into account that $E_2^{\text{cat}} = E_1^{\text{D}} - |\Delta E|$ and $E_2^{\text{an}} = E_1^{\text{D}} + |\Delta E|$, Eq. (10) can be written as [15]

$$\begin{aligned}
 I_{\text{ADPV}}^N &= \frac{I_{\text{ADPV}} \sqrt{\pi t_2}}{nFA \sqrt{D_A c_A^*}} \\
 &= \left\{ Z_2^{\text{cat}} + Z_2^{\text{an}} + \frac{\sqrt{\pi D_A t_2}}{r_0} (Z_2^{\text{cat}} \Omega_2^{\text{cat}} + Z_2^{\text{an}} \Omega_2^{\text{an}}) \right\} \\
 &\quad \times \left(1 + \frac{c_B^*}{\gamma c_A^*} \right) + \frac{(\gamma \mp 1) \sqrt{D_A t_2}}{\gamma r_0} \left(\frac{1 - K_1^{\text{D}} c_B^*/c_A^*}{1 + \gamma K_1^{\text{D}}} \right) \\
 &\quad \times (Z_2^{\text{cat}} + Z_2^{\text{an}}) W \left(\frac{t_2}{t_1} \right). \quad (11)
 \end{aligned}$$

In order to establish a quantitative comparison between both results (Eqs. (11) and (2), respectively) we must take into account that:

1. The value of the potential applied for the first pulse in the double pulse technique ADPV (E_1^{D}) must coincide with that of the second step applied in the triple-pulse technique DDPV (E_2), and the height of the step ($|\Delta E|$) must be identical in both techniques.
2. The duration of the second pulse, t_2 , in the double pulse technique ADPV must coincide with the duration of the third pulse, t_3 , corresponding to DDPV.
3. Once the equivalencies between $E_2^{\text{cat}} \rightarrow E_3$, $E_1^{\text{D}} \rightarrow E_2$ and $E_2^{\text{an}} \rightarrow E_1$, have been established, the values of Z_2^{cat} , Z_2^{an} , Ω_2^{cat} and Ω_2^{an} can be obtained directly from Eqs. (5) and (6). Specifically, $Z_2^{\text{cat}} = Z_3$, $Z_2^{\text{an}} = -Z_2$, $\Omega_2^{\text{cat}} = \Omega_3$ and $\Omega_2^{\text{an}} = \Omega_1$.

Under the above conditions Eq. (2) for the triple-pulse technique, DDPV, presents a great similarity to Eq. (11) for the double pulse technique, ADPV, with the exception of an additional term ($Z_3 Z_2 (1 + c_B^*/\gamma c_A^*) W(2/5)$) which appears in I_{DDPV}^N (Eq. (2)). Note that Eq. (2) has been obtained for the particular conditions $t_3 = 2t_2/3$ (i.e., $t_3/(t_2 + t_3) = 2/5$), since only in this situation is the expression corresponding to I_{DDPV}^N considerably simplified and can be easily compared with I_{ADPV}^N .

In Fig. 1 we have represented I_{DDPV}^N/E and I_{ADPV}^N/E curves corresponding to a spherical electrode of radius $r_0 = 0.02$ cm when B is soluble in electrolytic solution (Fig. 1(a)) and when B is amalgamated into the electrode (Fig. 1(b)), with $\gamma = 1$ in both cases. This figure shows that both techniques are coincident when B is soluble (Fig. 1(a)), as will be demonstrated below, and they present a qualitatively similar behaviour when amalgamation takes place (Fig. 1(b)). In this last case the peak currents obtained in ADPV are slightly higher in absolute value than those obtained in DDPV ($|I_{\text{ADPV}}^{\text{peak}}| > |I_{\text{DDPV}}^{\text{peak}}|$).

The identical behaviour of ADPV and DDPV with $t_3 = 2t_2/3$ shown in Fig. 1(a) for the particular case $D_A = D_B = D$ ($\gamma = 1$) and B soluble can be easily deduced by making $\gamma = 1$ and by taking the upper sign in Eqs. (2) and (11). Thus, under the equivalencies established above between potential pulses and the duration of each pulse, we obtain

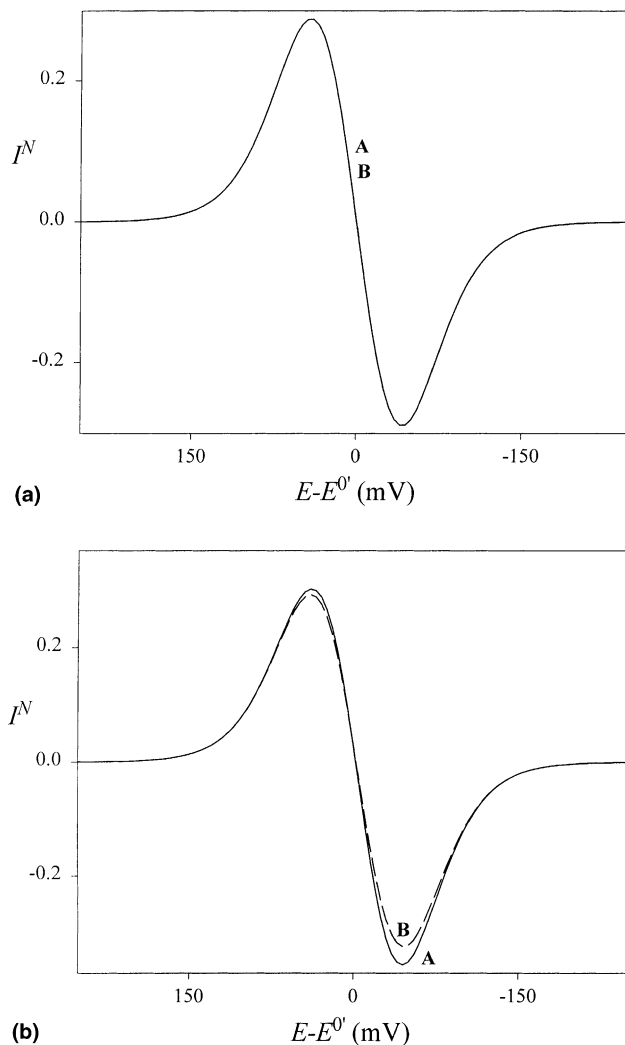


Fig. 1. I^N/E curves (with $E = E_1^{\text{D}}$ for ADPV and $E = E_2$ for DDPV) for a reversible process with $D_A = D_B$ ($\gamma = 1$) for: (a) B soluble in the electrolytic solution; (b) B amalgamated into the electrode, $n = 1$, $r_0 = 0.02$ cm, $c_B^* = 0$, $|\Delta E| = 50$ mV. Curves A correspond to ADPV (Eq. (11)) with $t_1 = 1$ s and $t_2 = 0.02$ s. Curves B correspond to DDPV (Eq. (2)) with $t_1 = 1$ s, $t_2 = 0.03$ s and $t_3 = 2t_2/3$.

$$\begin{aligned}
 I_{\text{ADPV}}^N &= I_{\text{DDPV}}^N \\
 &= \left(\frac{1}{1 + K_1^{\text{D}} e^{-\varepsilon}} - \frac{2}{1 + K_1^{\text{D}}} + \frac{1}{1 + K_1^{\text{D}} e^{\varepsilon}} \right) \\
 &\quad \times \left(1 + \frac{\sqrt{\pi D t_2}}{r_0} \right) \left(1 + \frac{c_B^*}{c_A^*} \right), \quad (12)
 \end{aligned}$$

where ε is given by Eq. (9) and t_2 is the duration of the second pulse in ADPV, identical to t_3 in DDPV.

This equation is of great interest since it signifies that under the above conditions, in I_{DDPV}^N and I_{ADPV}^N the effects of applied potentials, of the sphericity ($\sqrt{D t_2}/r_0$), and those of the relation of concentrations (c_B^*/c_A^*) can be independently analysed, since Eq. (12) can be written as

$$I_{\text{DDPV}}^N = I_{\text{ADPV}}^N = \theta(E_1^D, \varepsilon) \vartheta\left(\sqrt{Dt_2/r_0}\right) \rho(c_B^*/c_A^*) \quad (13)$$

with

$$\theta(E_1^D, \varepsilon) = \frac{1}{1 + K_1^D e^{-\varepsilon}} - \frac{2}{1 + K_1^D} + \frac{1}{1 + K_1^D e^{\varepsilon}},$$

$$\vartheta\left(\sqrt{Dt_2/r_0}\right) = 1 + \frac{\sqrt{\pi Dt_2}}{r_0}, \quad (14)$$

$$\rho(c_B^*/c_A^*) = 1 + \frac{c_B^*}{c_A^*}.$$

Eq. (13) is fulfilled for any value of the duration of the second pulse t_2 , for any value of the electrode radius and for any value of the initial concentrations of the electroactive species. Therefore, under these conditions, the values of peak potentials, E_M and E_m , and cross-potential, E_c , are independent of r_0 , of t_2 and of c_B^*/c_A^* . Hence, these potentials take identical values for planar electrodes ($r_0 \rightarrow \infty$) and for microelectrodes ($r_0 \rightarrow 0$). Moreover, from Eqs. (13) and (14) it is clear that $E_M - E^{0'} = -(E_m - E^{0'})$ and, consequently, for any electrode radius value

$$\left| \frac{I_M}{I_m} \right| = 1 \quad (15)$$

is fulfilled.

By making Eq. (12) zero, we obtain the characteristic point at which I_{DDPV}^N or I_{ADPV}^N bisect the abscissas axis for a potential value

$$E_c^{\text{sol}, \gamma=1} = E^{0'}. \quad (16)$$

It is also possible to obtain a simple expression for the difference between the peak potentials, E_M and E_m , which is given, for values of $|\Delta E| > 20$ mV and $n = 1$, by

$$\Delta E_{\text{ADPV}}^{\text{peak}} = \Delta E_{\text{DDPV}}^{\text{peak}} = E_M^{\text{sol}, \gamma=1} - E_m^{\text{sol}, \gamma=1}$$

$$\cong 67.68 + 7.44810^{-3} |\Delta E|^2$$

$$- 2.53810^{-7} |\Delta E|^4. \quad (17)$$

When $|\Delta E| < 10$ mV, it was fulfilled that

$$\Delta E_{\text{ADPV}}^{\text{peak}} = \Delta E_{\text{DDPV}}^{\text{peak}} = 68 \pm 0.3 \text{ mV}, \quad (18)$$

which coincides with the value obtained by Kim et al. for double derivative voltammetry in [16].

On the other hand, from Eq. (11) the expression for the current corresponding to the particular case of a plane electrode when the diffusion coefficients for both species are different ($\gamma \neq 1$) can easily be obtained by making $r_0 \rightarrow \infty$.

Fig. 2 shows the theoretical and experimental ADPV curves obtained for the system Fe(III) in oxalate for two different radius values of the SMDE. As can be seen, the concordance between theoretical and experimental results is very good. Moreover, the value of the cross-potential which coincides with $E^{0'}$ remains independent of the electrode sphericity in accordance with Eq. (12).

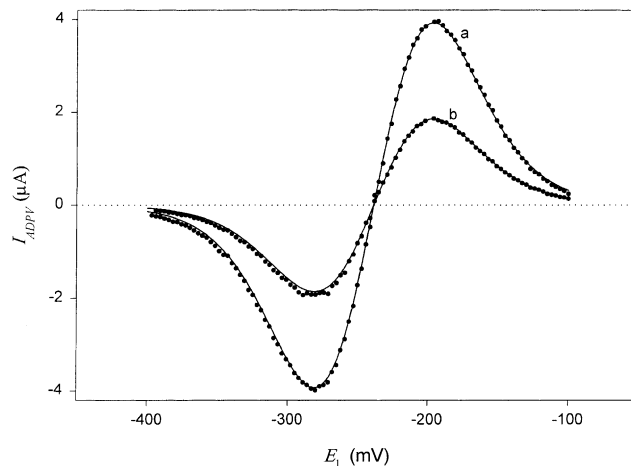


Fig. 2. Experimental (symbols lines) and theoretical (solid lines, Eq. (12)) I_{ADPV}/E_1 curves for 1 mM Fe^{3+} in 0.5 M $\text{K}_2\text{C}_2\text{O}_4$, pH = 4.45. $|\Delta E| = 50$ mV, $t_1 = 3$ s, $t_2 = 0.03$ s, $T = 291$ K, $D = 5.9 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, $E^{0'} = -238.5$ mV. The values of the electrode radii (in cm) are: (a) 0.038, (b) 0.026.

The data obtained in the above adjustment are $E^{0'} = 238 \pm 1$ mV and $D = (5.9 \pm 0.1) \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, both values are in good agreement with previous deduced in the literature [17].

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