Additive Differential Pulse Voltammetry for the Study of Slow Charge Transfer Processes at Spherical Electrodes

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Abstract

The application of additive differential pulse voltammetry to the study of the kinetics of a charge transfer process is studied. A simple analytical solution is presented, valid for spherical electrodes of any size and for electrode processes of any reversibility. From this solution, valuable diagnostic criteria for the elucidation of the electrochemical reversibility are established based on the variation of the ADPV signal with the duration of the potential pulses, the electrode radius and the pulse height. Working curves for the determination of the kinetic parameters are also given. The value of the ADPV technique is experimentally demonstrated by studying the kinetics of the reduction of 3-nitrophenolate− and europium3+ at mercury hemispherical microelectrodes.

Keywords: Additive differential pulse voltammetry, Slow charge transfer process, Heterogeneous rate constant, Transfer coefficient, Microelectrodes

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1 Introduction

In previous papers [1–4], double pulse technique additive differential pulse voltammetry (ADPV) has been developed and applied to different electrochemical problems. This technique is founded similar to differential double pulse voltammetry (DDPV) [5] but uses successive double potential pulses instead of triple pulses (see Figure 1). So, ADPV has a great advantage compared with DDPV since the ADPV signal is similar to the DDPV one but the mathematical treatment needed is much simpler. This is of special interest to study slow charge transfer processes for which the analytical solutions in DDPV are very awkward and difficult to apply.

Likewise, ADPV is a natural extension of differential pulse voltammetry (DPV) so that it does not require additional theoretical developments. The form of the signal in ADPV gives more information about the electrode processes, comprising two peaks with positive and negative values of the signal and a potential at which the ADPV signal is null (crossing potential), which can be experimentally measured with good precision. In addition, due to the definition of the technique the charging current effects are minimized to a large extent.

In the present paper, the application of the ADPV technique to the study of charge transfer processes with finite kinetics is performed. The influence of the electrode kinetics, the electrode size, the duration of the second potential pulse and the pulse height on the ADPV response are analyzed. From this, clear reversibility criteria are derived, founded on the variation of the ADPV curves with the above parameters. In addition, working curves are proposed as an additional tool for the extraction of the kinetic parameters from the variations of the crossing potential and the current of the maximum with the duration of the potential pulses.

For quasireversible processes with small values of the electron transfer coefficient (α < 0.4), two couple of peaks are observed in the ADPV response, at more positive and more negative potentials than the formal potential. This split of the signal into two is typical of differential techniques, being also observed for DPV [6], but it can give rise to misinterpretation of the experimental results by the unwary experimentalist.

Finally, the experimental application of the theory is carried out by characterizing the electrochemical reversibility of the reduction of 3-nitrophenolate− and Europium3+ on mercury hemispherical microelectrodes of ca. 25 μm radius.

2 Experimental

2.1 Chemical Reagents

Ferrocene (Fe(C5H5)2, Aldrich, 98%), hexaamminerruthenium(III) chloride ([Ru(NH3)6]Cl3, Aldrich, 98%), europium(III) chloride dihydrate (EuCl3, Aldrich, 99.99%), 3-nitrophenol (Ph(OH)NO2, Aldrich, 99%).
mercury(I) nitrate dihydrate (Hg₂(NO₃)₂, Aldrich, > 97%), acetonitrile (MeCN, Fischer Scientific, dried and distilled, 99%), dimethylsulfoxide (DMSO, Aldrich, anhydrous, 99.9%), tetra-n-butylammonium perchlorate (TBAP, Fluka, Puriss electrochemical grade, 99%), sodium perchlorate (NaClO₄, Sigma-Aldrich, 98 + %), tetra-n-butylammonium hexafluorophosphate (Bu₄NPF₆, Aldrich, 98%), potassium nitrate (KNO₃, Aldrich, 99 +% ACS reagent, 0.10 M), tetra-n-butylammonium hydroxide (Bu₄NOH, Sigma-Aldrich, 40 wt. % in water), perchloric acid (HClO₄, Aldrich, 70%) and nitric acid (HNO₃, Fisher Scientific, 70%, 0.15 M) were all used as received without further purification.

For the ADPV experiments 1 mM solutions of the oxidized species of the corresponding redox couple were prepared. The pH of Eu⁺⁺ solutions was fixed at 4.5 by addition of HClO₄. The solutions of 3-nitrophenolate monoanion were prepared in the electrochemical cell by addition of an excess of Bu₄NOH to 3-nitrophenol acid solutions [7].

2.2 Working Electrode

Mercury hemispheres were deposited chronoamperometically on Pt disc electrodes with \( r_0 = 25 \) µm from a degassed solution of \( \text{Hg}_2(\text{NO}_3)_2 \) (10 mM) with 0.1 M KNO₃ as supporting electrolyte (acidified with 0.5% of HNO₃), as described in literature [8,9]. Nitrogen atmosphere was maintained during the deposition.

The radius of the Pt disc was determined from the steady-state voltammogram of a 2 mM solution of Fc in acetonitrile containing 0.1 M TBAP, adopting a value of diffusion coefficient of ferrocene in MeCN of \( D = 2.3 \times 10^{-9} \text{ m}^2 \text{s}^{-1} \) at 25°C [10]. Prior to mercury deposition, the platinum electrode was polished using 3.0, 1.0, and 0.1 µm diamond spray on soft lapping pads (Kemet, UK). The size of the hemisphere was controlled by means of the amount of charge transferred (213.7 µC for \( r_0 = 25 \) µm). Next, the hemispherical geometry of the mercury deposit was established electrochemically by confirming that the ratio of the limiting steady-state currents of reduction of \( [\text{Ru(NH}_3\text{)}_6]^{3+} \) from cyclic voltammetry before and after deposition was close to \( \pi/2 \) [8].

Table 1. Definitions

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>( r_0 )</td>
<td>Radius of the electrode</td>
</tr>
<tr>
<td>( t_j ), ( j = 1, 2 )</td>
<td>Duration of the the ( j )-th potential pulse</td>
</tr>
<tr>
<td>( D )</td>
<td>Diffusion coefficient of the electroactive species</td>
</tr>
<tr>
<td>( c^*, i = O, R )</td>
<td>Bulk concentration of species ( i )</td>
</tr>
<tr>
<td>( k_r, k_n )</td>
<td>Heterogeneous rate constants of the reduction, oxidation processes</td>
</tr>
<tr>
<td>( k_i (= k^i (r_0/D)^{1/2}) )</td>
<td>Standard heterogeneous rate constant</td>
</tr>
<tr>
<td>( k^{\text{micro}} (= k^i r_0/D) )</td>
<td>Dimensionless rate constant at planar electrodes</td>
</tr>
<tr>
<td>( \alpha )</td>
<td>Dimensionless rate constant at microelectrodes under steady state conditions</td>
</tr>
<tr>
<td>( E^0 )</td>
<td>Transfer coefficient</td>
</tr>
<tr>
<td>( E_1, E_2 )</td>
<td>Formal potential of the electroactive couple</td>
</tr>
<tr>
<td>( E_{1a} = E_1 -</td>
<td>\Delta E</td>
</tr>
<tr>
<td>( E_{1b} = E_1 +</td>
<td>\Delta E</td>
</tr>
<tr>
<td>(</td>
<td>\Delta E</td>
</tr>
<tr>
<td>( E_c )</td>
<td>Pulse height</td>
</tr>
<tr>
<td>( I_{M} )</td>
<td>Crossing potential</td>
</tr>
<tr>
<td>( I_{p} )</td>
<td>Peak current corresponding to the positive peak</td>
</tr>
<tr>
<td>( I_{n} )</td>
<td>Peak current corresponding to the negative peak</td>
</tr>
</tbody>
</table>
### 2.3 Instrumentation

The mercury deposition, the calibration of the mercury hemispherical electrodes as well as the ADPV experiments were all undertaken with a computer-controlled Autolab potentiostat Type II (Eco-Chemie, Netherlands).

For the ADPV experiments a three-electrode set-up was employed, a 25 μm radius Hg electrode acting as working electrode and a coiled Pt wire as the counter electrode. As a reference electrode, a Saturated Calomel Electrode (SCE) was used for measurements in aqueous solution, whereas a commercial ‘no leak’ reference electrode comprising Ag/Ag⁺ in a PEEK barrel fitted with a membrane junction (66-EE009, Cypress electrodes) was employed for experiments in DMSO.

Before the application of each double pulse, the working electrode was open circuited for 10 s to restore the initial equilibrium conditions. Solutions were bubbled with N₂ before the ADPV experiments and positive pressure of N₂ was maintained throughout.

ADPV experiments in the absence of electroactive species were performed confirming in all cases that the background currents were not significant in the scales of potential and time of interest. The negligible effect of the iR-drop for the working conditions was also verified by numerical simulation [11].

### 3 Theory

We consider the application of ADPV to study the kinetics of a simple charge transfer reaction:

\[
O + e^- \xrightarrow{k_m} R
\]

(1)

In this technique, two differential pulse voltammograms are recorded, with negative values of the pulse height (normal mode) and with positive values of this parameter (reverse mode) (see Figure 1a). The differential pulse curves obtained are summed and plotted versus the first applied potential [1]. In Figure 1b the typical signal of ADPV is shown, together with the differential curves corresponding to normal and reverse modes (dashed lines). As can be seen, the ADPV response is characterized by two peaks, one positive maximum (Iₚ) and one negative minimum (Iₙ) and by the crossing potential (E_c) for which the signal is null (I_{ADPV}=0).

According with the description of the technique, the signal for ADPV is given by:

\[
I_{ADPV} = \Delta I_{\text{normal}} + \Delta I_{\text{reverse}}
\]

\[
= I_2(E_1-|\Delta E|) + I_1(E_1 + |\Delta E|) - 2I_1(E_1)
\]

(2)

Thus, from the analytical expressions obtained for DPV [6], an explicit analytical solution for the ADPV current is immediately deduced, valid for spherical electrodes of any size and whatever the kinetics of the electrode process:

\[
I_{ADPV} = k_m \frac{f_n(x_1)}{\theta_{z_2}} \left[ \frac{K_{z_2}^n}{\theta_{z_2}} + f_r(x_1) K_{z_2}^r \left[ \frac{1}{\theta_{z_2}} \cdot F(x_{z_2}/2) \right] \right]
\]

(3)

where the subscripts n and r refer to the normal and reverse mode, respectively, so that the second potential for the former is \(E_{z_2} = E_1 - |\Delta E|\) and for the latter \(E_{z_2} = E_1 + |\Delta E|\). All the variables and functions are given in the Appendix.

For the case of reversible processes (large \(k^0\) values), the above expression for the ADPV current simplifies to [1]:

\[
I_{ADPV} = \frac{1 + \mu}{1 + K_1} \left( \frac{K_1 - K_{z_2}^n}{1 + K_{z_2}^n} + \frac{K_1 - K_{z_2}^r}{1 + K_{z_2}^r} \right)
\]

(4)

Under these conditions it is found that, regardless of the value of the electrode radius, the pulse height and the duration of the potential pulses, the crossing potential coincides with the formal potential of the redox couple:

\[
E_c = E^0
\]

(5)

It is also interesting to note that, for reversible processes, the signal obtained in ADPV is identical to that in double differential pulse voltammetry (DDPV) for any electrode radius when the diffusion coefficients of both electroactive species are equal \((D_a = D_r = D)\) and it is fulfilled that \(I_1 = \frac{1}{2} I_2\), \(I_{DDPV} = I_{ADPV}^\text{plane}\), \(E_1^\text{DDPV} = E_{P_{ADPV}}^\text{plane}\), \(E_2^\text{DDPV} = E_{P_{ADPV}}^\text{plane}\) and \(E_3^\text{DDPV} = E_{z_2}^\text{ADPV}\) [1].

### 3.1 Particular Cases

From Equation 3, expressions under some interesting conditions can be derived:

- **Planar electrodes** (\(r_0 \to \infty\)). Expression 3 becomes:

\[
I_{ADPV,\text{plane}} = \frac{1}{1 + K_1} \left( \frac{K_1 - K_{z_2}^n}{1 + K_{z_2}^n} + \frac{K_1 - K_{z_2}^r}{1 + K_{z_2}^r} \right)
\]

(6)

and the expression for the ADPV current of reversible processes is given by:

\[
I_{ADPV} = \frac{(1 + \mu) \left( K_1 - K_{z_2}^n \right)}{1 + K_{z_2}^n + K_1 - K_{z_2}^r}
\]

(7)

– Ultramicroelectrodes (UME). When \( r_0 \ll (\pi D_0)\frac{1}{2} \), Equation 3 tends to:

\[
\frac{I_{ADPV}}{I_d(\infty)} = \frac{k_{\text{micro}}}{k_{\text{micro}}} \left[ \frac{K_{2,0}^{-1}(1 - \mu K_{2,0}) + K_{2,0}^{-1}(1 - \mu K_{2,0})}{\theta_{2,0}} - 2 K_{1}^{-1}(1 - \mu K_{1})/\theta_{1} \right]_{(\theta)} \]  

(8)

A time-independent response is obtained so that the current registered at each potential pulse is not affected by the previous ones. Thus, under steady state conditions the ADPV response is equivalent to that obtained in DPV whatever the reversibility of the process.

For the case of reversible systems, the expression for the ADPV current at hemispherical ultramicroelectrodes is:

\[
\frac{I_{ADPV}}{I_d(\infty)} = \frac{(1 + \mu)}{(1 + K_{1})} \left\{ \frac{K_{1} - K_{2,0}}{1 + K_{2,0}} + \frac{K_{1} - K_{2,1}}{1 + K_{2,1}} \right\} \]  

(9)

Note that for reversible systems the influence of the electrode sphericity and the applied potentials are separate (see Equations 4, 7 and 9) like in DPV. As a consequence, the same normalized \( I_{ADPV}/I_{d,0} \) vs. \( E \) curves (with \( I_{d,0} = I_d(\infty)(1 + r_0(\pi D_0)^{-1/2}) \)), and therefore the same peak and crossing potentials, are obtained whatever the electrode size [1].

4 Results and Discussion

In Figure 2 the influence of the kinetic parameters \( (k^0, \alpha) \) on the ADPV curves are modelled at a spherical microelectrode \( (\xi_s = 0.2) \). In general terms, the peak currents decrease and the crossing and peak potentials shift towards more negative values as the electrode processes is more sluggish (see Figure 2a). For quasireversible systems \( (k^0 = 10^{-2}-10^{-4} \text{ cm/s}) \), the peak currents are very sensitive to the value of the heterogeneous rate constant \( k^0 \) whereas the variation of the crossing potential is less apparent. On the other hand, for totally irreversible processes \( (k_s = 10^{-4} \text{ cm/s}) \), the crossing potential significantly shifts towards more negative values, whereas the peak currents are independent of the \( k^0 \) value.

The relative symmetry of the peaks also indicates the degree of reversibility; thus, for reversible systems symmetrical peaks are obtained (i.e., \( |I_{s}/I_m| = 1 \)) whereas for quasireversible and irreversible processes \( |I_{s}/I_m| > 1 \).

In Figure 2b, the influence of the electron transfer coefficient \( (\alpha) \) on the ADPV curve is shown. A decrease of \( \alpha \) gives rise to the decrease of the peak currents together with the shift of the peak and crossing potentials towards more negative values. The ratio of the peak currents \( (|I_{s}/I_m|) \) also varies with \( \alpha \) such that the greater the \( \alpha \) value, the greater the \( |I_{s}/I_m| \) ratio.

It is worth highlighting the anomalous shape of the ADPV signal found for small \( \alpha \) values (see curve for \( \alpha = 0.3 \) in Figure 2b). Under this situation, two pairs of peaks are found, a small one situated at more positive values than the formal potential and a larger one at more negative values. Thus, two peaks with \( I_{ADPV} > 0 \), two peaks with \( I_{ADPV} < 0 \) and three crossing potentials are obtained. The appearance of a new signal at more positive potentials is related to the great influence of the anodic contribution when the \( \alpha \) value is very small. The split into two of the response for quasireversible systems is typical of differential techniques and it has been previously described for differential pulse voltammetry (DPV) at which a double peak is obtained for small \( \alpha \) values (\( \alpha \leq 0.3 \)) [6].

In Figure 3 the variation of the ADPV voltammogram with the electrode size is considered for the three general cases of reversible, quasireversible and irreversible systems. For a reversible process (Figure 3a), the dimensionless current \( I_{ADPV}/I_0^{\alpha}(D_0) \) increases when the electrode radius decreases, whereas the crossing and peak potentials are independent of the electrode size. On the other hand, for quasireversible (Figure 3b) and irreversible (Figure 3c) systems, the crossing and peak potentials vary with the electrode size so that the smaller the electrode, the more negative their values. Thus, the reversibility of
the process can be evaluated from the variation of the crossing potential of the ADPV curves with the electrode radius.

The dotted curves in Figure 3 correspond to an ultramicroelectrode and in the three cases they are identical to those obtained in the DDPV technique when $t_3 = \frac{1}{2} t_2$.

$$I_{\text{ADPV}} = I_{\text{DDPV}} = I_{\text{ADPV}} \quad E_{1,\text{DDPV}} = E_{2,\text{ADPV}} \quad E_{2,\text{DDPV}} = E_{1,\text{ADPV}} \quad \text{and} \quad E_{3,\text{DDPV}} = E_{2,\text{ADPV}} [1].$$

The influence of the pulse height ($|\Delta E|$) on the ADPV curves is analyzed in Figure 4. For any reversibility degree, the crossing potential is independent of the $|\Delta E|$ value. With respect to the symmetry of the peaks, the ratio $|I_m|/I_m$ is practically unaffected by $|\Delta E|$ for fast

Fig. 3. Influence of the electrode size on the ADPV curves for reversible ($k^2 = 1 \text{ cm/s, Figure 3.a, Eq. 4}$), quasireversible ($k^2 = 10^{-2} \text{ cm/s, Figure 3.b, Eq. 3}$) and irreversible ($k^2 = 10^{-3} \text{ cm/s, Figure 3.c, Eq. 3}$) systems. Three electrode sizes are considered: planar electrodes ($\xi_2 = 0$, —), microelectrodes ($\xi_2 = 0.4$, ——) and ultramicroelectrodes ($\xi_2 = 1.0$, ·····) at $a = 0.5$, $t_1/t_2 = 50$. Other conditions as in Figure 2.

Fig. 4. Influence of the pulse height ($|\Delta E|$) on the ADPV curves for reversible ($k^2 = 1 \text{ cm/s, Figure 4.a, Eq. 4}$), quasireversible ($k^2 = 10^{-2} \text{ cm/s, Figure 4.b, Eq. 3}$) and irreversible ($k^2 = 10^{-3} \text{ cm/s, Figure 4.c, Eq. 3}$) systems. Three $|\Delta E|$ values are considered: 75 mV (——), 50 mV (—) and 25 mV (·····). $\xi_2 = 0.4$. Other conditions as in Figure 3.
electrode kinetics whereas for slow charge transfer processes (Figures 4b and 4c), the pulse height does affect this ratio so that this increases with $|\Delta E|$. In Figure 5 the variation of $|I_m/I_0|$ with the pulse height is plotted for different electrode kinetics, showing that the influence of the pulse height is more apparent for slow electrode processes.

The durations of the potential pulses ($t_1, t_2$) are also valuable parameters of the ADPV technique for kinetic studies. In Figure 6 the variation of the ADPV curves with $t_2$ are plotted and compared with numerical results. It is worth highlighting the excellent agreement existing between the analytical (Equation 3) and numerical results even for long $t_2$ values.

In this figure it is also observed that for slow electrode processes there is a shift of the voltammogram towards more positive potentials as the duration of the second pulse ($t_2$) is longer, which is related with more reversible behaviour. On the other hand, for faster charge transfers the position of the voltammogram, and so the crossing potential, are almost independent of $t_2$.

The variation of the current corresponding to the positive maximum ($I_M$) and the negative minimum ($I_m$) with the duration of the second pulse also gives us information about the electrode kinetics. In Figure 7 the behaviours of $I_M$ (solid line) and $I_m$ (dashed line) with $t^{-1/2}$ are plotted for different electrode kinetics. For a reversible process (Figure 7a), both $I_M$ and $I_m$ has a characteristic linear relationship with $t^{-1/2}$ for any electrode radius, which does not hold for quasi-reversible (Figure 7b) or totally irreversible (Figure 7c) systems. In addition, the variation of $I_m$ with $t^{-1/2}$ is much smaller for sluggish charge transfers.

Note that the evaluation of the electrochemical reversibility by means of the behaviour of the crossing potential and the peak currents with $t_2$ is very simple since ADPV curves at different $t_2$ values can be obtained from a single experiment.

For the quantitative determination of the kinetic parameters, working curves are given in Figures 8 and 9 based on the variation of the crossing potential ($E_c$) and the current corresponding to the maximum ($I_m$) with the duration of the double potential pulse ($t_1 + t_2$).

Regarding the crossing potential, $E_c$ varies towards more anodic values (Figure 8) as $\xi$ increases, this varia-
tion being dependent on the value of the transfer coefficient (Figure 8b). For fast charge transfers (large $k_{\text{micro}}$ values), the crossing potential is less sensitive to the electrode kinetics (see Figure 2) so that for this case the maximum current is more adequate for kinetic studies (Figure 9).

From these working curves the kinetic parameters of the electrode process ($k^0$ and $\alpha$) can be determined from ADPV experiments carried out with different values of the durations of the pulses (i.e., different $\xi_2$ values), keeping the ratio $t_1/t_2$ constant.

The experimental application of the above results was performed by studying the electrochemical reversibility of two one-electron reduction processes:

- 3-nitrophenolate $^{\text{-2}}$:  
  \[
  \text{[Ph(O^-)NO}_2 \text{]}^- + e^- \overset{k_{\text{micro}}}{\rightleftharpoons} \text{[Ph(O^-)NO}_2 \text{]}^{\text{-1}}
  \]  
  (I)

- Eu$^{3+}/2+$:  
  \[
  \text{Eu}^{3+} + e^- \overset{k_{\text{micro}}}{\rightleftharpoons} \text{Eu}^{2+}
  \]  
  (II)

These redox couples enable to cover very different electrode kinetics [12–16]. For ADPV experiments, de-
Slow Charge Transfer Processes at Spherical Electrodes


Fig. 9. $I_d/I_p(t_2)$ vs. log $\xi_2$ working curves for several $k^{\text{micro}}$ values (marked on the curves). Eq. 3, $\alpha = 0.5, t_1/t_2 = 50, |\Delta E| = 50$ mV.

gassed 1 mM solutions of the oxidized species of the corresponding redox couple (i.e., 3-nitrophenolate$^{--2\cdot}$, Europium$^{3\cdot+}$) were prepared under the conditions detailed in Table 2.

In Figure 10 the experimental ADPV curves obtained at mercury hemispherical electrodes with $r_e=25 \mu m$ are shown. From simple analysis of the signals, qualitative information about the kinetics of the electrode process can be extracted. Thus, it is observed that the curve corresponding to 3-nitrophenolate$^{--2\cdot}$ system (black points) has two almost symmetrical peaks and a crossing potential very close to the formal potential. Both features in the ADPV curves are indicating a fast charge transfer reaction.

On the other hand, the ADPV curve obtained for Eu$^{3\cdot+}$ (grey points) is much more shifted towards negative potentials with respect to $E^0$ and it shows a greater asymmetry of peaks, from which it can be inferred that the electron transfer is more sluggish (see Table 2).

The determination of the kinetic parameters for both systems has also been performed by following the methodology proposed in Figures 8 and 9. Thus, ADPV experiments with different durations of the potential pulses (keeping constant the ratio $t_1/t_2$) were recorded and the values of the crossing potential and the current corresponding to the maximum were determined and plotted versus the $\xi_2$ parameter.

According to the results above discussed, for the study of the faster electrode reactions (i.e., 3-nitrophenolate$^--$, Figure 11a) the variation of $I_d$/$I_p(t_2)$ with $\xi_2$ is more suitable to characterize the electrode kinetics, whereas for the more sluggish process (i.e., Eu$^{3\cdot+}$, Figure 11b) the shift of the crossing potential is more adequate. So, by single point fit of the corresponding theoretical and experimental curves (see Figure 11), the values of the heterogeneous rate constant ($k^0$) and the electron transfer coefficient ($\alpha$) for both systems were determined (Table 2). The fitting was done by computerized minimum least square procedure, the value of the sum of the squared residuals ($S$) being indicated on the curves as an indicator of the goodness of the fitting.

By comparing the data of the kinetic parameters extracted from the ADPV experiments (Table 2) with those reported in the literature with different electrochemical techniques (Table 3), a good or reasonable concordance is found which validates the theoretical development as well as the value of the ADPV technique for the characterization of the electrode kinetics.

Table 2. Heterogeneous rate constant ($k^0$) and transfer coefficient ($\alpha$) corresponding to the best fit of the theoretical (Eq. 3) and experimental ADPV results (see Figures 10 and 11).

<table>
<thead>
<tr>
<th>Redox Couple</th>
<th>Medium [a]</th>
<th>$D \times 10^6$ (cm$^2$ s$^{-1}$) [d]</th>
<th>$k^0$ (cm$^2$ s$^{-1}$)</th>
<th>$\alpha$</th>
<th>$E^0$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-Nitrophenolate$^{--2\cdot}$</td>
<td>0.1 M Bu$_4$NPF$_6$, DMSO</td>
<td>3.30 ± 0.03</td>
<td>$1.9 \times 10^{-3}$</td>
<td>0.45 [e]</td>
<td>$-1.415$ [e]</td>
</tr>
<tr>
<td>Eu$^{3\cdot+}$/H$^+$</td>
<td>0.1 M NaClO$_4$, H$_2$O (pH 4.5)</td>
<td>6.11 ± 0.05</td>
<td>$2.3 \times 10^{-4}$</td>
<td>0.72</td>
<td>$-0.643$ [b]</td>
</tr>
</tbody>
</table>

[a] Concentration substrate: 1 mM of 3-nitrophenolate$^-$, Eu$^{3\cdot+}$; [b] vs. Ag/Ag$^+$ reference electrode [11]; [c] vs. Ag/Ag$^+$ reference electrode [11]; [d] calculated from several repeat potential step chronoamperograms; [e] value calculated from the fit of the complete ADPV curve.
Conclusions

The value of additive differential pulse voltammetry for the study of the electrode kinetics of a charge transfer process is shown. An explicit analytical solution is derived for processes with finite kinetics at spherical electrodes of any size, from planar electrodes to hemispherical ultramicroelectrodes.

The crossing potential \( E_c \) and the peak currents \( I_M, I_m \) of the ADPV signal are sensitive to the reversibility of the electrode process. Thus, the electrochemical reversibility of the system can be easily evaluated from the variation of \( E_c, I_M \) and \( I_m \) with the duration of the second potential pulse, the electrode radius and the pulse height. Moreover, the comparison of theoretical and experimental values for \( E_c \) and \( I_M \) assists the extraction of the kinetic parameters.

The experimental validation of the theory was also carried out by studying the kinetics of the reduction of 3-nitrophenolate\(^{–\cdot} \) (fast charge transfer) and Europium\(^{3+} \) (slow charge transfer) on mercury microhemispheres.

Appendix

Functions and variables

\[
F(x) = \exp(x^2) \cdot \text{erfc}(x)
\]  
\[
\mu = \frac{c_0^N}{c_0^{1/2}}
\]  
\[
I_d(\infty) = \frac{F A c_0^N D}{r_0}
\]  
\[
I_m^P(t_2) = \frac{F A c_0^N \sqrt{D}}{\sqrt{\pi t_2}}
\]  
\[
\eta_j = \frac{F}{RT} (E_j - E_0^j), \quad j \equiv 1, 2(n, r)
\]  
\[
K_j = \exp(\eta_j), \quad j \equiv 1, 2(n, r)
\]  
\[
\theta_1 = 1 + k^{\text{micro}} K_1^{-1}(1 + K_1)
\]  
\[
\theta_{2m} = 1 + k^{\text{micro}} K_2^{-1}(1 + K_2)
\]  
\[
\chi_1 = \frac{x_1}{E^0 - E^0_0}
\]  
\[
S = 2 \sqrt{\frac{D \cdot (t_1 + t_2)}{r_0}}
\]  

Table 3. Data reported in the literature for the diffusion coefficient \( D \), heterogeneous rate constant \( k^j \) and electron transfer coefficient \( \alpha \) of the systems under study at mercury electrodes. DCV: derivative cyclic voltammetry; DPP: differential pulse polarography; SWV: square wave voltammetry.

<table>
<thead>
<tr>
<th>Redox couple</th>
<th>Medium</th>
<th>( D \times 10^9 ) (cm(^2) s(^{-1}))</th>
<th>( k^j \times 10^5 ) (cm(^2) s(^{-1}))</th>
<th>( \alpha )</th>
<th>Method</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-Nitrophenolate(^{–\cdot} )</td>
<td>0.1 M BuNPF(_6^) DMSO</td>
<td>4.0</td>
<td>2.1 \times 10^{-2}</td>
<td>0.43</td>
<td>DCV</td>
<td>[12]</td>
</tr>
<tr>
<td></td>
<td>1 M NaClO(_3^) ( \text{H}_2\text{O} ) (pH 3.0)</td>
<td>7.0</td>
<td>2.5 \times 10^{-4}</td>
<td>0.60</td>
<td>DC polarography</td>
<td>[13]</td>
</tr>
<tr>
<td></td>
<td>0.3 M NaClO(_3^) ( \text{H}_2\text{O} )</td>
<td>–</td>
<td>9.3 \times 10^{-5}</td>
<td>0.68</td>
<td>Chrono-coulometry</td>
<td>[14]</td>
</tr>
<tr>
<td></td>
<td>1 M KCl, ( \text{H}_2\text{O} )</td>
<td>–</td>
<td>2.6 \times 10^{-4}</td>
<td>0.54</td>
<td>DPP</td>
<td>[15]</td>
</tr>
<tr>
<td></td>
<td>0.1 M NaClO(_3^) ( \text{H}_2\text{O} ) (pH 2.0)</td>
<td>–</td>
<td>10^{-3}</td>
<td>0.76</td>
<td>SWV</td>
<td>[16]</td>
</tr>
<tr>
<td></td>
<td>1 M NaClO(_3^) ( \text{H}_2\text{O} )</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>Chrono-potentiometry</td>
<td>[17]</td>
</tr>
</tbody>
</table>


\[ \chi_1 = 2 \sqrt{\frac{t_1 + t_2}{D}} K_1^{-\alpha} (1 + K_1) = (\chi_1)_{\xi_1=0} \]  

(A11)

\[ \chi_2 = \xi_2 + \chi_2^D, \quad m = n, r \]  

(A12)

\[ \xi_2 = \frac{2 \sqrt{D \cdot t_2}}{r_0} \]  

(A13)

\[ \chi_3 = 2 \sqrt{\frac{r_2}{D}} K_2 \chi_2^D (1 + K_2) = (\chi_2)_{\xi_2=0}, \]  

(A14)

\[ m = n, r \]

\[ f_m(x) = 1 - \mu K_{2m} \]  

\[ -(1 - \mu K_1) \left( \frac{K_{2m}}{K_1} \right)^{\alpha} \left( \frac{\theta_{2m}}{\theta_1} + \left( \frac{1 - \theta_{2m}}{\theta_1} \right) \cdot F(x) \right), \]  

(A15)

\[ m = n, r \]

\[ f_m^\alpha(x) = 1 - \mu K_{2m} \]  

\[ -(1 - \mu K_1) \left( \frac{1 + K_{2m}}{1 + K_1} \right) \left[ 1 + \left( \frac{1 + K_1}{1 + K_{2m}} \right)^{-\alpha} - 1 \right] \cdot F(x), \]  

(A16)

\[ m = n, r \]

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**References**