Theoretical and experimental study of Differential Pulse Voltammetry at spherical electrodes: Measuring diffusion coefficients and formal potentials

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Rigorous and approximate analytical expressions are deduced for Differential Pulse Voltammetry at spherical electrodes of any size, including microelectrodes, when the electrogenerated species is soluble in the electrolytic solution. From these, we examine the utility of DPV for the determination of diffusion coefficients and formal potentials, establishing the optimum conditions for this purpose. The experimental validation of the theoretical results is reported for mercury microelectrodes of ca. 50 and 10 \( \mu \)m diameters both in aqueous and ionic liquid media.

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\textbf{1. Introduction}

Differential Pulse Voltammetry (DPV) is based on the application of successive double potential pulses as shown in Fig. 1. This technique is one of the most suitable to characterize electrochemical systems since it presents a peak-shaped response with the nonfaradaic contribution and the ohmic drop effect significantly reduced as compared to alternative procedures [1–3].

In this paper, we present a simple expression for DPV for the case that the second potential pulse is much shorter than the first one, based on explicit equations previously deduced for Double Potential Step Chronoamperometry at spherical electrodes [4]. This analytical solution takes a very simple form and is immediately applicable to electrodes of any size, from planar to microspherical. Moreover, the case of unequal diffusion coefficients of the oxidized and reduced species is considered so that it is possible to establish the optimal conditions for the determination of both diffusion coefficients and the formal potential by means of DPV experiments. In particular, whereas the peak potential depends on both diffusion coefficients for all electrode radii, the peak current is more sensitive to the electrode product diffusion coefficient on medium-size microelectrodes, when the reduced species is not present in bulk solution.

Experimental validation of the analytical theoretical results reported for mercury hemispherical microelectrodes. Diffusion coefficients and formal potential values for diverse redox systems are obtained, emphasising the value of the DPV technique for these studies both in conventional solvents and in Room Temperature Ionic Liquids (RTILs), where significant difference in the diffusion coefficients of the reductive and oxidative components of a redox couple are often encountered.

RTILs are composed entirely of ions (a bulky, asymmetric organic cation and a weakly coordinate inorganic or organic anion) and exist in the liquid phase at and around room temperature. Recently, they have been used increasingly as replacements for conventional molecular solvents in many fundamental research applications due to their favourable chemical and physical properties, such as high chemical and thermal stability, intrinsic electrical conductivity, near-zero volatility and wide electrochemical potential windows. Due to the higher viscosity of RTILs compared to the more conventional solvents, e.g. water, acetonitrile, diffusion coefficients of the electroactive species are lowered accordingly. Moreover, notably unequal diffusivities of reduced and oxidized species are found [5–8] so that the results herein presented are very useful in these new solvents.
2. Experimental

2.1. Chemical reagents

Ferrocene (Fe(C₅H₅)₂, Aldrich, 98%), cobaltocenium hexafluorophosphate (Co(C₅H₅)₂PF₆, Acros Organics, 98%), hexaammineruthenium(III) chloride ([Ru(NH₃)₆]Cl₃, Aldrich, 98%), octaazabicyclo[6.6.6]eicosane cobalt(III) trichloride ([CoSep]Cl₃, Aldrich, 95%) acetonitrile (MeCN, Fischer Scientific, dried and distilled, 99%), tetra-n-butylammonium perchlorate (TBAP, Fluka, Puriss electrochemical grade, 99%), mercury(I) nitrate dihydrate (Hg₂(NO₃)₂, Aldrich, >97%), potassium nitrate (KNO₃, Aldrich, 99% ACS reagent, 0.1 M) and nitric acid (HNO₃, Fisher Scientific, 70%, 0.15 M) were all used as received without further purification. 1-Ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide, [C₂mim][NTf₂], was prepared according to standard literature procedures [9]. 1-Butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide tetrafluoroborate, [C₄mim][BF₄], and 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide hexafluorophosphate, [C₄mim][PF₆], were kindly donated by Merck KGaA and used as received.

See Scheme 1 for the structures of the RTILs and compounds used.

2.2. Electrodes

Mercury was electrodeposited on Pt disc electrodes with \( r_0 = 25 \, \mu m \) and \( r₀ = 5 \, \mu m \) from a 10 mM solution of Hg₂(NO₃)₂ with 0.1 M KNO₃ as supporting electrolyte (acidified with 0.5% of HNO₃), as described in literature [10,11]. Before the mercury deposition procedure was undertaken, the platinum electrode was polished using 3.0, 1.0, and 0.1 \( \mu m \) diamond spray on soft lapping pads (Kemet, UK), and calibrated by analyzing the steady-state voltammetry of a 2 mM solution of Fe in acetonitrile containing 0.1 M TBAP, to give the electrode diameter, adopting a value of diffusion coefficient of ferrocene in MeCN of \( D = 2.3 \times 10^{-9} \, m^2 \, s^{-1} \) at 25 °C [12].

The mercury nitrate solution was bubbled with nitrogen gas (BOC, Guildford, Surrey, UK) for 30 min to remove atmospheric oxygen, and then mercury was deposited chronopotentiometrically by holding the potential at −0.245 V utilising a coiled Pt wire as a counter electrode and an Ag wire as the reference electrode. Next, the hemispherical geometry of the mercury deposit was confirmed electrochemically by demonstrating that the ratio of limiting steady-state currents of reduction of [Ru(NH₃)₆]³⁺ from cyclic voltammetry before and after deposition was close to \( \pi/2 \).

2.3. Instrumentation

2.3.1. Mercury hemispherical electrode deposition and calibration

A computer-controlled \( \mu \)-Autolab potentiostat Type II (Eco-Chemie, Netherlands) was used to undertake the mercury deposition as well as calibration of the platinum disc and mercury hemispherical electrodes. DPV experiments were performed with a homebuilt potentiostat designed to apply the corresponding waveform (Fig. 1a and b). Before the application of each double pulse, the working electrode was open circuited for 5 s in order to restore equilibrium conditions.

All experiments were undertaken at 298 ± 1 K in a heated Faraday cage.

2.3.2. DPV experiments in water solutions

For measurements in aqueous solutions, a three-electrode set-up was employed, with a 25 \( \mu m \) radius Hg electrode as working electrode, a Ag/AgCl reference electrode and a coiled Pt wire as the counter electrode. Solutions were bubbled with N₂ before and during experiments.

Fig. 1. Differential Pulse Voltammetry. (a) Potential–time function; note that after each double pulse, the initial equilibrium conditions are restored (indicated with double slash); (b) technique parameters; (c) current samples; (d) DPV signal.
3. Theory

We consider a reversible charge transfer reaction:

\[ O + n e^- \rightleftharpoons R \]  

(1)

when a double potential pulse is applied at a stationary spherical electrode, assuming that the reduced species is soluble in the electrolyte solution, and that the diffusion coefficients of the electroactive species may be different.

The applied potential is set at a value \( E_1 \) in the interval \( 0 \leq t \leq t_1 \) and stepped from \( E_1 \) to \( E_2 \) at the time \( t \geq t_1 \) (i.e., \( t = t_1 + \tau_2 \); \( 0 \leq \tau_2 \leq t_2 \) (see Scheme 1). For this problem we derived in Ref. [4] the general expression for the current at any values of \( E_1 \) and \( E_2 \):

\[
I_2 = I_1(t_1 + \tau_2) + I_{d2}(\tau_2) \cdot \left( \frac{1 + (cK_1/\gamma \cdot c_0)}{1 + \gamma K_1} \right) \left[ 1 + \gamma \cdot \Omega_2 \cdot \zeta_2 \right] + I_{d2}(\tau_2) \cdot Z_{1,2} \cdot P_1 \left\{ 1 + \gamma \cdot \Omega_2 \cdot \zeta_2 \right\} \left[ 1 - F(\zeta_1) \right] + \frac{\gamma \cdot \zeta_2 \cdot Y_{1,2} \cdot S^{rev}(\xi, \zeta_1) + \frac{\gamma \cdot \zeta_2 \cdot S^{diff}(\xi, \zeta_1)}{\sqrt{\pi}} \right\}
\]

(2)

with:

\[
I_1(t) = I_{d1}(t) \left\{ \frac{1 - (cK_1/\gamma \cdot c_0)K_1}{1 + \gamma K_1} \right\} \left[ 1 + \sqrt{\pi} \frac{D_0 \cdot I_0}{t_0} \left( 1 + \gamma \cdot K_1 \right) \right]
\]

(3)

where the variables and functions are given in Appendix A.

The above expressions are fully general, being valid for any spherical electrode size (including planar electrodes and ultramicroelectrodes), for any \( \gamma \) value and for all potential pulse times \( (t_1, t_2) \).

In DPV technique two current samples are measured, one at the end of the first pulse \( (I_1(t_1)) \) and another one at the other end of the second pulse \( (I_2(t_1 + t_2)) \), where \( t_2 << t_1 \), and the DPV curve is a plot of the difference between the two current samples \( (\Delta I = I_2(t_1 + t_2) - I_1(t_1)) \) versus a potential \( x-axis \). The first potential pulse value \( (E_1) \) is generally chosen as \( x-axis \) potential. However, in this paper we will choose the arithmetic average of both potential values \( (E_{1,2} = (E_1 + E_2)/2) \), see Scheme 1) as the \( x-axis \) potential, pointing out below some consequences of this choice.

Considering that in DPV the initial equilibrium conditions are restored after each double pulse (Fig. 1a), the theory for double pulse voltammetry fully applies to this technique. Thus, from the rigorous general solution (Eq. (2)) it is possible to obtain a simpler expression for DPV technique by making \( x \rightarrow 0 \) \( (t_2 << t_1) \), from which analysis of the response is greatly simplified. Thus, making \( x \rightarrow 0 \) in Eq. (2),

\[
\Delta I = I_{d2}(\tau_2) \cdot Z_{1,2} \cdot \left( 1 + \gamma \cdot \Omega_2 \cdot \zeta_2 \right) \left[ 1 + \frac{cK_1}{\gamma c_0} \right] + \frac{(\gamma - 1)(1 - cK_1/c_0)(1 - F(\zeta_1))}{(1 + \gamma K_1)}
\]

(4)

where

\[
\zeta_1' = \frac{2\sqrt{D_0 \cdot t_1}}{t_0 \cdot I_1}
\]

(5)

According to expression (4), the DPV curves depend on the diffusion coefficients of both species \( (D_0, D_0) \), the pulse height \( (\Delta \zeta) \) through \( K_1 \) and \( K_2 \), the electrode radius \( (r_0) \) and the pulse durations \( (t_1, t_2) \). Moreover, it is worth highlighting that under these conditions, the expression for DPV curves contains the function \( F(\zeta_1') \) an infinite power series of \( \zeta_1' \) (sphericity parameter), while previous solutions [14–17], which contain only a few terms, are approximate solutions, not valid for small electrodes.

The applicability of expression (4) is dependent on the ratio \( t_1/ t_2 \), and on the electrode size. So, the radius range of validity of this expression broadens when the ratio \( t_1/t_2 \) increases. For example, for \( 2 \sqrt{D_0 \cdot t_1}/r_0 < 3.2 \), \( t_1/t_2 = 50 \) and \( \gamma \rightarrow 1/5 \) the error of Eq. (4) is lower than 1% in the DPV curves in the region around the DPV peak.

3.1. Particular cases

From Eq. (4) expressions for some interesting conditions can be easily derived as follows:

- **Planar electrodes** \( (r_0 \rightarrow \infty) \). When \( \zeta_1' \rightarrow 0 \) \( (F(\zeta_1') \rightarrow 1) \) and \( \zeta_2 \rightarrow 0 \), the expression (4) becomes:
\[ \Delta F_{\text{plane}} = I_{e2} \cdot Z_{12} \cdot \left( 1 + \frac{C_k}{\gamma C_0} \right) \]
\[ = \frac{nFAC_0}{\sqrt{\pi D_0}} \left( \gamma + \frac{C_k}{C_0} \right) \frac{K_1 - K_2}{(1 + \gamma K_2)(1 + \gamma K_1)} \] (6)

- **Ultramicroelectrodes (UME).** When \( r_0 < \sqrt{\pi D_0 t_2}; \quad i = 0, R \), Eq. (2) tends to that corresponding to steady state conditions so that the DPV response simplifies to:
\[ \Delta F_{\text{UME}} = \frac{nFAC_0}{r_0} \left( \gamma + \frac{C_k}{C_0} \right) \frac{K_1 - K_2}{(1 + \gamma K_2)(1 + \gamma K_1)} \] (7)

Note that reaching a steady state response requires extremely small electrodes (\( r_0 < 10^{-6} \text{ m} \) for \( t_1 = 1 \text{ s}, t_2 = 0.02 \text{ s} \) and \( D_0 = 10^{-9} \text{ m}^2 \text{s}^{-1} \)).

- **Equal diffusion coefficients** \( D_0 = D_1 = D \). From Eq. (4) by making \( \gamma = 1 \) it is deduced that:
\[ \Delta F_{\gamma = 1} = \frac{nFAC_0}{\sqrt{\pi D_0}} \left( 1 + \sqrt{\frac{\pi D_0}{r_0}} \right) \frac{K_1 - K_2}{(1 + K_2)(1 + K_1)} \] (8)

This equation is generally applicable, so that, for \( t_1 / t_2 \gg 50 \) the error is lower than 0.2% in the region around DPV peak for any electrode size.

We are using in this paper a potential axis at which we take the average of the two stepped potentials \( (E_{1,2} = \frac{E_{1,2}}{2}) \) instead of the usual \( E_1 \)-value. Note that this choice gives the advantage that the peak potential coincides with the half-wave potential (as occurs in Square Wave Voltammetry, SWV) regardless of the electrode radius, although DPV curves are much easier to analyze than SWV ones. Moreover, for a given experimental system (electrode geometry, diffusion coefficients) the DPV curves corresponding to a negative pulse height (\( \Delta E < 0 \), normal mode) and to a positive one (\( \Delta E > 0 \), reverse mode) are fully symmetrical with respect to the potential axis for planar electrodes (Eq. (6)), ultramicroelectrodes (Eq. (7)) and when both diffusion coefficients are equal (Eq. (8)).

### 3.2. Peak potential and peak current

For the particular cases studied in Section 3.1, it is possible to obtain simple analytical expressions for the values of peak potential and peak current. The peak potential \( (E_{\text{peak}}) \) is obtained by equalizing to zero the derivative \( d\Delta F/dE_{1,2} \). Next, by substituting \( E_{\text{peak}} \) in the expression for \( \Delta F \), we immediately deduce that for the peak current \( (\Delta I_{\text{peak}}) \).

In all the cases, the expression for the current separates into two factors, one dependent on \( t_2 \) and/or \( r_0 \) and another one dependent on \( \gamma, E_1, E_2 \). As only the second factor varies “along” DPV scan, the peak potential is only a function of the parameters included in this factor, and so is independent of time-geometry parameters.

- **Planar electrodes:**
\[ E_{\text{peak, plane}}^{1,2} = E^0 + \frac{RT}{nF} \ln \left( \frac{1}{\gamma} \right) = E_{E_{\text{plane}}}^{1/2} \] (9)
\[ \Delta I_{\text{peak, plane}}^{1,2} = -\frac{nFAD_0 C_0}{\sqrt{\pi D_0}} \left( 1 + \frac{C_k}{\gamma C_0} \right) \tanh \left( \frac{nF \Delta E}{RT} \frac{1}{4} \right) \] (10)

The peak potential corresponds to the “reversible” half-wave potential \( (E_{E_{\text{plane}}}^{1/2}) \), whose value depends on the \( \gamma \) value, allowing determination of \( D_k \) once \( D_0 \) is known.

- **Ultramicroelectrodes:**
\[ E_{\text{peak, UME}}^{1,2} = E^0 + \frac{RT}{nF} \ln \left( \frac{1}{\gamma} \right) = E_{E_{\text{UME}}}^{1/2} \] (11)
\[ \Delta I_{\text{peak, UME}}^{1,2} = -\frac{nFAD_0 C_0}{r_0} \left( 1 + \frac{C_k}{\gamma C_0} \right) \tanh \left( \frac{nF \Delta E}{RT} \frac{1}{4} \right) \] (12)

As in the planar electrode case, at ultramicroelectrodes the value of the peak potential coincides with the “reversible” half-wave potential \( (E_{E_{\text{UME}}}^{1/2}) \) from which it is also possible to determine \( D_k \).

- **Equal diffusion coefficients** \( D_0 = D_k = D \):
\[ E_{\text{peak, plane}}^{1,2} = E^0 \] (13)
\[ \Delta I_{\text{peak, plane}}^{1,2} = -\frac{nFAD_0 C_0}{\sqrt{\pi D_0}} \left( 1 + \sqrt{\frac{\pi D_0}{r_0}} \right) \left( 1 + \frac{C_k}{\gamma C_0} \right) \tanh \left( \frac{nF \Delta E}{RT} \frac{1}{4} \right) \] (14)

The peak potential value corresponds to the formal potential value for any electrode radius.

From Eqs. (9) and (11) it can be deduced that the \( \gamma \) influence on the peak potential in DPV increases from planar electrodes to spherical ultramicroelectrodes, with intermediate behaviour expected for spherical electrodes. So, the smaller the electrode radius, the greater the separation between the peak potentials corresponding to different \( \gamma \) values. For a given \( \gamma \) value, the peak potential varies between the value at planar electrodes \( (E_{\text{peak, plane}}^{1,2}) \) and the value at ultramicroelectrodes \( (E_{\text{peak, UME}}^{1,2}) \), being the difference:
\[ \Delta E_{\text{peak}}^{1,2} = E_{\text{peak, UME}}^{1,2} - E_{\text{peak, plane}}^{1,2} = \frac{RT}{nF} \ln \left( \frac{1}{\gamma} \right) = E_{E_{\text{plane}}}^{1/2} \] (15)

From this equation it is concluded that a decrease in the electrode radius leads to a shift of the peak potential towards more positive potentials when \( \gamma < 1 \), and towards more negative potentials when \( \gamma > 1 \), with the magnitude of this shift increasing as the diffusion coefficients become more different. Therefore, \( \Delta E_{\text{peak}} \) value may be used to determine \( \gamma \) value. Note that when \( \gamma = 1 \) the peak potential value is the same for any electrode radius \( (\Delta E_{\text{peak}}^{1,2} = 0) \) and is equal to the formal potential (Eq. (13)).

Regarding the initial presence of the reduced species \( (c_2) \), this does not have any influence on the peak potential value (see Eqs. (9), (11), and (13)), but its effect on the peak current is very relevant (see Eqs. (10), (12), and (14)). The peak current increases with the initial concentration of species R; besides, as can be deduced from Eqs. (10) and (12), the initial concentration of species R determines the dependence of \( \Delta E_{\text{peak}} \) with respect to species R diffusion coefficient \( (D_k) \) at planar electrodes and ultramicroelectrodes. Thus, when \( c_2 = 0 \) the peak current value increases when \( D_k \) increases, whereas when species R is not initially present \( (c_2 = 0) \) the peak current does not depend on \( D_0 \) value. This last case will be further discussed in the following section.

### 4. Discussion and results

#### 4.1. Theoretical results

In Fig. 2 we have studied the influence of \( \gamma \) on the DPV curves at three electrode sizes when only the oxidized species is initially present. With respect to the peak potential, it can be observed that,

- for any electrode radius, a decrease of \( \gamma \) (that is, an increase of \( D_k \)) leads to a shift of the peak potential towards more positive potentials,
- this effect being more obvious with smaller electrode radii.

As was previously stated, the peak current at planar electrodes and ultramicroelectrodes are independent of \( D_k \) when \( c_2 = 0 \) (Fig. 2a and c). Therefore, neither planar electrodes nor spherical...
Fig. 2. DPV curves when only oxidized species is initially present for three electrode sizes: planar electrode (a), from Eq. (6)), spherical electrode with $r_0 = 5 \times 10^{-3}$ m (b), from Eq. (4)) and ultramicroelectrode with $r_0 = 5 \times 10^{-6}$ m (c), from Eq. (7)). Five $\gamma$ values are considered: $\gamma^2 = 1/5$ (— — — —), $\gamma^2 = 1/2$ (– – – – – ), $\gamma^2 = 1$ (—), $\gamma^2 = 2$ (– – – – – ) and $\gamma^2 = 5$ (– – – – – – ). $\Delta E = +50 \text{ mV}$, $E_{1/2}^{\text{final}} - E^0 = +150 \text{ mV}$, $E_{1/2}^{\text{initial}} - E^0 = -150 \text{ mV}$, number of points = 50. $t_1 = 1 \text{ s}$, $t_2 = 0.02 \text{ s}$, $c_1 = 1 \text{ mM}$, $c_2 = 0 \text{ mM}$, $D_0 = 10^{-9} \text{ m}^2 \text{s}^{-1}$. $I_{d, \text{planar}}(t_1) = nFAC_0 / \sqrt{D_0 / \pi \gamma^2}$. 

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ultramicroelectrodes allow determination of both the diffusion coefficients \( (D_O, D_R) \) from \( \Delta I^{\text{peak}} \) values. At spherical electrodes (Fig. 2b), however, the peak current does depend on \( D_R \) value so that \( \Delta I^{\text{peak}} \) increases when \( D_R \) decreases. There exists a range of values of electrode radii at which the effect of \( \gamma \) is maximum and so the sensitivity to \( D_R \) is optimal. It is observed that the radius values corresponding to the highest sensitivity depend on the ratio \( t_2/t_1 \) and \( D_O/D_R \) and correspond approximately to the value \( r_0 \approx \sqrt{D_O t_1}, \) that is, approximately the planar diffusion layer thickness of species O.

In Fig. 3 we show the influence of the electrode radius on the peak potential. In order to better show the radius effect, the DPV curves are normalized, i.e., \( \Delta I/\Delta I^{\text{peak}} \). As mentioned above, when \( \gamma > 1 \) a decrease of electrode radius gives rise to a shift of the peak potential. Three electrode sizes are considered: planar electrode (—, from Eq. (6)), \( r_0 = 2 \times 10^{-5} \) m (— — — —, from Eq. (4)), \( r_0 = 5 \times 10^{-5} \) m (—, from Eq. (7)). \( \gamma \) values are marked on the curves. Other conditions as in Fig. 2.

![Graph](image)

**Fig. 3.** Influence of electrode radius on the peak potential. Three electrode sizes are considered: planar electrode (—, from Eq. (6)), \( r_0 = 2 \times 10^{-5} \) m (— — — —, from Eq. (4)), \( r_0 = 5 \times 10^{-5} \) m (—, from Eq. (7)). \( \gamma \) values are marked on the curves. Other conditions as in Fig. 2.

![Graph](image)

**Fig. 4.** (a) DPV curves corresponding to a scan in normal mode \( (\Delta E = -50 \text{ mV}) \) and in reverse mode \( (\Delta E = +50 \text{ mV}) \) at a spherical electrode \( (r_0 = 2 \times 10^{-5} \text{ m}, \text{from Eq. (4)}) \). Three \( \gamma \) values are considered: \( \gamma^2 = 1/5 \) (— — — —), \( \gamma^2 = 1 \) (—) and \( \gamma^2 = 5 \) (— — —). (b) variation of \( \Delta I^{\text{peak}}_2 \) with the ratio of diffusion coefficients. \( E_{1,2}^{\text{initial}} - E_0^{(2)} = +200 \text{ mV}, E_{1,2}^{\text{final}} - E_0^{(2)} = -200 \text{ mV}, \) number of points = 70. Other conditions as in Fig. 2.

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potential towards more negative potentials, whereas when \( \gamma < 1 \) the shift is towards more positive potentials. For \( \gamma = 1 \), the peak potential is independent of the electrode size and equal to the formal potential (Eq. (13)). According to Eq. (15), under the conditions considered in the figure (\( \gamma^2 = 5, 1/5 \)) the absolute value of the difference between the peak potential at planar electrode and a spherical ultramicroelectrode is \( |E_{\text{peak,ultramicro}} - E_{\text{peak,plane}}| \approx 20.7 \text{ mV} \).

Fig. 4 shows DPV curves corresponding to a negative pulse height (\( \Delta E < 0 \)) and to a positive one (\( \Delta E > 0 \)) for three \( \gamma \) values at a spherical electrode. For any \( \gamma \) value, the peak potential is the same for normal and reverse modes when \( E_{1,2} \) is chosen as the x-axis.

The sign of \( \Delta E \) has an influence on \( \Delta E_{\text{peak}} \), and this depends on the ratio of the diffusion coefficients of electroactive species. We define:

\[
\Delta E_{\text{peak}}^D = \frac{|\Delta E_{\text{peak}}(\Delta E > 0) - \Delta E_{\text{peak}}(\Delta E < 0)|}{|\Delta E_{\text{peak}}(\Delta E > 0) + \Delta E_{\text{peak}}(\Delta E < 0)|}
\]  

As can be seen in Fig. 4, \( \Delta E_{\text{peak}}^D = 1 \) when both diffusion coefficients are equal (\( D_O = D_R \)) (see Eq. (12)), when \( D_O > D_R \), \( \Delta E_{\text{peak}}^D > 1 \), whereas when \( D_O < D_R \) we find that \( \Delta E_{\text{peak}}^D < 1 \). So, this ratio is sensitive to the \( \gamma \) value and, therefore, is very useful for the determination of diffusion coefficients. It has also been observed that the greater \( t_1/t_2 \) ratio, and pulse height “\( \Delta E \)”, the greater sensitivity of \( \Delta E_{\text{peak}}^D \).

4.2. Experimental DPV study on hemispherical Hg microelectrode

As discussed above, DPV curves are sensitive to diffusion coefficients and to the formal potential of the redox couple, so that it is possible to obtain information about these parameters from peak potential and peak current values. Experimental validation of the theoretical aspects outlined in Section 4.1, and of the value of DPV for the determination of electrochemical parameters were performed in different media using a mercury hemisphere as the working electrode.

DPV curves were recorded both in aqueous media and in RTILs for several redox couples. Electrode radius, pulse durations and pulse height values were chosen in order to obtain DPV curves of good sensitivity reflecting the deductions in the previous section from the analytical solution.

For each case, the diffusion coefficient of oxidized species (\( D_O \)) was determined from chronoamperometric measurements under cathodic limiting conditions by using the equation below [1,2]:

\[
I_d = \frac{nFAc_d D_0}{r_0} + \frac{nFAC_0}{D_0} \sqrt{\frac{\pi t}{A}}
\]

where \( A = 2\pi r_0^2 \).

With \( D_O \) known, the diffusion coefficient of reduced species (\( D_R \)) was determined by fitting analytical and experimental peak current values. Finally, the formal potential was obtained from the peak potential value. For the fit of experimental and theoretical
DPV results, the ratio $\Delta E_{p}^{\text{peak}}$ was used since this is sensitive to the diffusion coefficient of the reduced species (see Section 4.1), and presents the important advantage of being much less affected by the value of the electrode radius than the peak current “$I_{p}$”, so that the tolerance to the uncertainty of $r_{0}$ value is much higher.

Experimental and best-fitted analytical DPV curves are plotted in Fig. 5. The agreement between them is very satisfactory, validating the theory herein presented and the feasibility of DPV technique to obtain information of electrochemical parameters in conventional and ionic liquid media.

Data corresponding to the best fit between analytical and experimental results are summarized in Table 1. $D_{0}$ and $D_{0}/D_{0}$ ratios well compare with previous reports and are in agreement with results formerly reported in the literature [5–8]. As mentioned previously, differences of up to 2 orders of magnitude are found between diffusion coefficients values in water and in ionic liquids due to an increase in the viscosity. Moreover, considerably unequal diffusivities of reduced and oxidized species are found in RTILs, with $D_{0}/D_{0}$ ratios more than 1; this was also noted by Rogers et al. [7] using cyclic voltammetry and double potential step chronoamperometric analysis in a variety of ionic liquids on a Pt electrode, and suggests that uncharged species (cobaltocene) diffuses faster likely because of weaker interactions with the composing ions. So, we can infer that in RTILs the electrostatic interactions of the solute with the solvent have a fundamental role on its transport properties, so that the presence of charge has a significant influence on the magnitude of the diffusion coefficient. Thus, besides the classical hydrodynamic considerations, the extent of these interactions must be taken into account to properly analyze these systems [20–23].

5. Conclusions

Simple analytical expressions for Differential Pulse Voltammetry at spherical electrodes have been presented, in particular covering the case when the oxidized and reduced species have unequal diffusion coefficients. Successful experimental validation of the theoretical results both in water and RTILs was performed.

From the theoretical and experimental results, DPV proves to be a valuable technique for determination of diffusion coefficients and formal potentials under the appropriate conditions, which optimally involve the use of medium-size microelectrodes in conventional solvents and of ultramicroelectrodes in RTILs for greatest sensitivity. The authors greatly acknowledge Mr. Philip Hurst for the development of the potentiostat for the DPV experiments. We thank Leigh Aldous and Prof. Christopher Hardacre of Queens University, Belfast, for donating the RTILs. A.M., F.M.-O., C.S. and E.L. greatly appreciate the financial support provided by the Dirección General de Investigación (MEC) (Project Number CTQ2006-12552/BQU) and by the Fundación SEN- ECA (Expediton Number 03079/P0/05). Also, E.L thanks the Ministerio de Ciencia e Innovacion for the grant received. E.I.R. and N.V.R. thank the EPSRC and J.G.L.-P. the CONACYT (Mexico) for funding.

**Table 1**

Diffusion coefficients and formal potentials obtained from DPV experiments.

<table>
<thead>
<tr>
<th>Redox couple</th>
<th>Medium</th>
<th>$D_{0}$ (m$^{2}$ s$^{-1}$)</th>
<th>$D_{0}/D_{1}$</th>
<th>$E_{p}$ (mV)</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ru(NH$_3$)$<em>6$]$</em>{3+}$/2$^{+}$</td>
<td>aq. 0.1 M KNO$_3$</td>
<td>(7.15 ± 0.04) x 10$^{-10}$</td>
<td>1.12</td>
<td>−150$^a$</td>
<td>[18,19]</td>
</tr>
<tr>
<td>[Co(sepi)]$^{3+}$/2$^{+}$</td>
<td>aq. 0.1 M KNO$_3$</td>
<td>(7.29 ± 0.01) x 10$^{-10}$</td>
<td>1.01</td>
<td>−515$^a$</td>
<td>[24]</td>
</tr>
<tr>
<td>[Co(C$_2$H$_5$)$<em>2$]$</em>{20}$</td>
<td>[C$_2$ mim][NTf$_2$]</td>
<td>(3.61 ± 0.04) x 10$^{-11}$</td>
<td>1.18</td>
<td>−1330$^a$</td>
<td>[7]</td>
</tr>
<tr>
<td>[Co(C$_2$H$_5$)$<em>2$]$</em>{10}$</td>
<td>[C$_4$ mim][BF$_4$]</td>
<td>(9.58 ± 0.02) x 10$^{-12}$</td>
<td>1.16</td>
<td>−1329$^a$</td>
<td>[7]</td>
</tr>
<tr>
<td>[Co(C$_2$H$_5$)$<em>2$]$</em>{10}$</td>
<td>[C$_4$ mim][PF$_6$]</td>
<td>(3.83 ± 0.02) x 10$^{-12}$</td>
<td>1.53</td>
<td>−1334$^a$</td>
<td>[7]</td>
</tr>
</tbody>
</table>

$^a$ Vs. Ag/AgCl, KCl(sat).

$^b$ Vs. internal reference Fc$^+$/Fc.

$^c$ Error bars calculated from the standard deviation of the best theoretical fits from several repeat potential step chronoamperograms.

**Appendix A. Notation and definitions**

\[
F(x) = e^{(x/2)2} \cdot \text{erfc}(x/2) \tag{A1}
\]

\[
\xi_1 = \frac{2\sqrt{D_{k}(\tau_1 + \tau_2)}}{r_{0}D_{1}} \tag{A2}
\]

\[
\xi_2 = \sqrt{\frac{D_{0} \cdot D_{k} \cdot \tau_2}{r_{0}}} \tag{A3}
\]

\[
I_{d1}(t_1 + \tau_2) = \frac{nFAC_0\sqrt{D_{0}}}{\sqrt{\pi(t_1 + \tau_2)}} \tag{A4}
\]

\[
I_{d2}(\tau_2) = \frac{nFAC_0\sqrt{D_{0}}}{\sqrt{\pi t_2}} \tag{A5}
\]

\[
\eta_i = n F (E_{i} - E^0) \quad i \equiv 1, 2 \tag{A6}
\]

\[
K_i = \exp(\eta_i) \quad i \equiv 1, 2 \tag{A7}
\]

\[
\Omega_i = \frac{1 + K_i}{1 + \gamma K_i} \quad i \equiv 1, 2 \tag{A8}
\]

\[
J_i = \frac{1 + \gamma K_i}{\tau_{0} K_i + 1} \quad i \equiv 1, 2 \tag{A9}
\]

\[
Z_{12} = \frac{\gamma(K_1 - K_2)}{(1 + \gamma K_1)(1 + \gamma K_2)} \tag{A10}
\]

\[
Y_{12} = \frac{K_2(\gamma - 1)(\gamma J_2 - 1)J_2^2}{(1 + \gamma K_2)J_2^2} \tag{A11}
\]

\[
P_i = \frac{(\gamma - 1)(1 - (C_0/C_2)K_1)}{(\gamma^2 K_1 + 1)} \tag{A12}
\]

\[
G(x) = x \cdot \arcsin(x) + \sqrt{1 - x^2} \tag{A13}
\]

\[
\xi = \frac{\tau_2}{\tau_1 + \tau_2} \tag{A14}
\]

\[
\gamma = \left(\frac{D_0}{D_k}\right)^{1/2} \tag{A15}
\]
\[ S^{\text{sum}}(\alpha, \xi_1) = \sum_{i=2}^{\infty} \left( \frac{(-1)^{j-i} \cdot (\xi_1)^j \cdot 2^i j}{i \prod_{l=1}^{i-1} P_l} \right) A \]

\[ S^{\text{odd}}(\alpha, \xi_1) = \sum_{i=1}^{\infty} \left( \frac{(-1)^{j-i} \cdot (\xi_1)^j \cdot 2^{j-i+1} \cdot P_i \cdot B}{(i+1) \prod_{l=1}^{i} P_l} \right) \]

being:

\[
\text{if } 2j < i: \quad A = \frac{\prod_{l=0}^{i-1}(i-2l)}{2^i \cdot j!} \left[ 1 - (\frac{1}{j_2})^{j-j-1} \right]
\]

\[
\text{if } 2j = i: \quad A = \frac{\prod_{l=0}^{i-1}(i-2l)}{2^i \cdot j!} \sum_{l=0}^{\frac{i-1}{2}} \left( \frac{1}{j_2} \right)^{2l} \left[ (j-l)! \left( \frac{1}{j_2} \right)^{j-1} \right]
\]

where the sum is only effective for \( i \geq 2 \).

\[
\text{if } 2j > i:
\begin{align*}
\text{i odd:} & \quad A = \frac{\prod_{l=0}^{i-1}(i-2l)}{2^i \cdot j!} \sum_{l=0}^{\frac{i-1}{2}} \left( \frac{1}{j_2} \right)^{2l} \left( \frac{j-1}{j_2} \right) \left( \frac{j-l}{j_2} \right)^{j-1} \\
\text{i even:} & \quad A = 0
\end{align*}
\]

\[
\text{if } 2j + 1 < i:
\begin{align*}
B & = \frac{\prod_{l=0}^{i-1}(i-2l+1)}{(2j+1) \cdot 2^i \cdot (j+1)!} \left[ 1 - \left( \frac{1}{j_2} \right)^{j+1} \right]
\end{align*}
\]

\[
+ Y_{1,2} \sum_{m=0}^{\frac{i-1}{2}} \left( -1 \right)^m \cdot 2^m \left( \frac{j_2}{j_2} \right)^{2m+1} \prod_{l=0}^{m+1} \left( \frac{j-1}{j_2} \right) \left( \frac{j-k+1}{j_2} \right)^{2k-1}
\]

where the sum is only effective for \( j \geq 1 \).

\[
\text{if } 2j + 1 > i:
\begin{align*}
\text{i odd:} & \quad B = \frac{\prod_{l=0}^{i-1}(i-2l+1)}{(2j+1) \cdot 2^i \cdot (j+1)!} \left[ 1 - \left( \frac{1}{j_2} \right)^{j+1} \right] + Y_{1,2} \sum_{m=0}^{\frac{i-1}{2}} \left( -1 \right)^m \cdot 2^m \left( \frac{j_2}{j_2} \right)^{2m+1} \prod_{l=0}^{m+1} \left( \frac{j-1}{j_2} \right) \left( \frac{j-k+1}{j_2} \right)^{2k-1}
\end{align*}
\]

\[
\times \left( \frac{1}{j_2} \right)^{j-j-1} \left( \frac{j-1}{j_2} \right) \left( \frac{j-l}{j_2} \right)^{j-1}
\]

\[
\text{i even:} & \quad B = 0
\]

References


