Reverse Pulse Voltammetry at spherical electrodes: Simultaneous determination of diffusion coefficients and formal potentials. Application to Room Temperature Ionic Liquids

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ABSTRACT

A rigorous analytical solution for Reverse Pulse Voltammetry (RPV) at spherical electrodes of all sizes is presented, including the case where the diffusion coefficients of the electroactive species are different. From this solution, the value of RPV for the determination of both diffusion coefficients and the formal potential of the redox couple is demonstrated. The experimental application of the theoretical results is carried out both in ionic liquids and in aqueous solution with mercury microelectrodes of ca. 50 and 10 μm diameters. The former solvent system is of particular interest due to the great importance of these new liquids in which notably unequal diffusion coefficients are commonly found.

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1. Introduction

The Reverse Pulse Voltammetry (RPV) technique consists of successive double potential pulses so that the first step corresponds to diffusion-limiting conditions (E1 → −∞ if considering a reduction process) and the second potential (E2) varies towards more positive values as shown in Fig. 1 [1,2]. RPV is very suitable for studying the product of the electrode reaction – generated during the first pulse –, and in particular for the determination of the diffusion coefficients of the electroactive species.

Despite the above, hitherto there was not an analytical solution for the appropriate study with RPV of systems where the reactant and the product species have different diffusivities (D0 ≠ D1), since those existing in the literature are partial solutions, only valid for large electrodes [3–6]. In a previous paper [7], a general expression for a double potential pulse at spherical electrodes for all values of γ ([ ] / [ ]) was deduced. From this, a rigorous analytical solution for RPV can be obtained by imposing the corresponding potential-time conditions (Fig. 1a), permitting us to perform the study of RPV technique. Thus, the feasibility of the simultaneous determination of the diffusion coefficients of both electroactive species and the formal potential in a single RPV experiment is demonstrated, and the optimal conditions for this purpose are established.

Note that the results herein presented are of remarkable practical interest, since there are numerous systems where the supposition D0 = D1 (γ = 1) is not correct and gives rise to very meaningful errors. Among these systems, it is worth highlighting the case of Room Temperature Ionic Liquids (RTILs), where the diffusion coefficients of the oxidized and the reduced species are often rather different [8–11].

The interest of RTILs as an alternative to conventional solvents has largely increased in recent years because of their favourable properties, such as high chemical and thermal stability, intrinsic electrical conductivity, near-zero volatility and wide electrochemical potential windows. Due to the potential application in this area, the experimental validation of RPV technique for the determination of electrochemical parameters is performed both in RTILs and in aqueous solution.

An interesting comparison of RPV and Normal Pulse Voltammetry (NPV) techniques with the electrode size, varying from ultramicroelectrodes to planar ones, is also included. This analysis is of great interest to understand the physical meaning of the corresponding current–potential curves. Indeed, although both responses have identical form, they only become indistinguishable practically at ultramicroelectrodes when the steady state is reached so that memory of the first pulse is lost.

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2. Experimental

2.1. Chemical reagents

Ferrocene (Fe(C₅H₅)₂, Aldrich, 98%), cobaltocenium hexafluorophosphate (Co(C₅H₅)₂PF₆, Acros Organics, 98%), hexaaamineruthenium(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, 0.10 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 [12]. 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 structures of the RTILs and compounds used.

2.2. Electrodes

Mercury was electrodeposited chronoamperometrically on Pt disc electrodes with \( r_0 = 25 \) μm and \( r_0 = 5 \) μm from a degassed solution of Hg₂(NO₃)₂ as described in the literature [13,14]. The potential was held at −0.245 V and a coiled Pt wire was used as counter electrode and an Ag wire as reference electrode.

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), and the steady-state voltammetry of a ferrocene solution was recorded to give the electrode diameter, adopting a value of diffusion coefficient of ferrocene in MeCN of \( D = 2.3 \times 10^{-5} \text{ cm}^2 \text{s}^{-1} \) at 25 °C [15].

The ratio of limiting steady-state currents of reduction of [Ru(NH₃)₆]³⁺ from cyclic voltammetry before and after deposition was close to \( p = 2 \), indicating that the geometry of the mercury deposit is hemispherical [13,14].

2.3. Instrumentation

A computer-controlled μ-Autolab potentiostat Type II (Eco-Chemie, Netherlands) was used for deposition and calibration of mercury hemisphere.

RPV experiments were performed with a homebuilt potentiostat designed to apply the corresponding waveform (Fig. 1a and b). Before the application of each double pulse, equilibrium conditions were restored by open circuiting the working electrode for 10 s.

For RPV experiments in aqueous solutions, a three-electrode set-up was employed, with a 25 μm radius Hg electrode as the working electrode, Ag/AgCl reference electrode and a coiled Pt wire as the counter electrode. Solutions were bubbled with N₂ before experiments to remove atmospheric oxygen and a positive pressure of N₂ maintained throughout.

In ionic liquids, a 5 μm radius Hg hemisphere was used as the working electrode, with a silver wire quasi-reference electrode, and these were housed in a T-cell [16] specially designed to study small volumes of RTIL solutions under a controlled atmosphere. A 10 mM ferrocene internal reference couple was employed to avoid the potential shift of a quasi-reference electrode affecting the results [10]. The liquid was purged under vacuum for 2 h prior to and during experiments.
The current is measured at the end of the second pulse (at a value corresponding to cathodic limiting current (23)).

Let us consider the following reversible charge transfer reaction:

$$\text{O} + ne^- \rightleftharpoons R$$  \hspace{1cm} (1)

when a double potential pulse is applied at a stationary spherical electrode, assuming that the reduced species is soluble in the electrolytic solution and including the case of unequal diffusion coefficients ($D_0 \neq D_6$).

According to RPV waveform (Fig. 1), the applied potential is set at a value corresponding to cathodic limiting current ($E_1 \rightarrow -\infty$) in the interval $0 < t < t_1$ and stepped from $E_1$ to $E_2$ at the time $t > t_1$. The current is measured at the end of the second pulse ($t = t_1 + t_2$) and plotted vs. the second potential value (see Fig. 1d). After each double pulse, the initial equilibrium conditions are re-established.

In a previous paper [7], we obtained the expression for the current corresponding to the application of a double potential step at spherical electrodes for all $E_1, E_2$ values. From this expression, that corresponding to RPV technique is immediately obtained by making $E_1 \rightarrow -\infty$:

$$I_{RPV} = I_{d1}(t_1 + t_2) + P_{d2}(t_2) \cdot Z_2[1 + (C_j/\gamma \cdot C_0)](1 + \gamma \cdot \Omega_2 \cdot \xi_2) + (\gamma - 1) \cdot P_{d2}(t_2) \cdot Z_2[(1 + \gamma \cdot \Omega_2 \cdot \xi_2)[1 - F(\xi_1)]$$

$$+ \frac{\xi_1}{\sqrt{\pi}} \left[ G(\xi) - 1 \right] + \gamma \cdot \xi_2 \cdot Y_2 \cdot S^\text{red}(\xi_1) + \frac{\xi_2}{\sqrt{\pi}} \cdot S^\text{odd}(\xi_1) \right\}$$

(2)

where $I_{RPV}$ refers to the current at $t = t_1 + t_2$ and all the variables and functions are defined in the Appendix.

The solution deduced is general so that it can be applied to electrodes of any radius, including the following limit cases:

- **Planar electrodes** ($r_0 \rightarrow \infty$), when $\xi_1 \rightarrow 0$ ($F(\xi_1) \rightarrow 1$) and $\xi_2 \rightarrow 0$ the expression for the current is given by:

$$I_{\text{plane}} = nFAC_0\sqrt{D_0}\left( \frac{1}{\sqrt{(t_1 + t_2)}} - \frac{1}{\sqrt{(t_1 + t_2) [1 + \gamma \cdot K_2]}} \right)$$

(3)

- **Spherical ultramicroelectrodes** ($UME$, $r_0 \ll \sqrt{\pi D_2 t_2}$: $i \equiv 0, R$), Under these conditions we checked that the second pulse does not depend on the first one:

$$I_{\text{UME}} = \frac{nFAC_0 D_0}{r_0} \left( 1 - \frac{K_2}{1 + \gamma \cdot K_2} \right)$$

(4)

### 3.1. The oxidized species only present in bulk solution ($C_0 = 0$)

**3.1.1. Cathodic limiting current, $I_{d,DC}$** ($E_2 \rightarrow -\infty$, $K_2 \rightarrow 0$)

By making $Z_2 \rightarrow 0$ the expression for the cathodic limiting current at spherical electrodes is obtained [1,2]:

$$I_{d,DC} = I_{d1}(t_1 + t_2) + P_{d2}(t_2) \left[ 1 + \frac{\sqrt{\pi D_0 (t_1 + t_2)}}{r_0} \right]$$

(5)

As expected, $I_{d,DC}$ is not sensitive to the diffusion coefficient of species R, and only depends on that of the oxidized species.

**3.1.2. Anodic limiting current, $I_{d,RPV}$** ($E_2 \rightarrow +\infty$, $K_2 \rightarrow +\infty$)

Under these conditions it is fulfilled that $Y_2 \rightarrow 0$, $Z_2 \rightarrow -1$ and $\Omega_2 \rightarrow 1/\gamma$ so that:

$$I_{d,RPV} = I_{d1}(t_1 + t_2) - P_{d2}(t_2)(1 + \xi_2) - (\gamma - 1) \cdot P_{d2}(t_2)$$

$$\cdot \left\{ (1 + \xi_2)[1 - F(\xi_1)] + \frac{\xi_1}{\sqrt{\pi}} [G(\xi) - 1] + \frac{\xi_2}{2\sqrt{\pi}} \cdot S(\xi_1, \xi) \right\}$$

(6)

where:

$$S(\xi_1, \xi) = \sum_{i=1}^{\infty} \frac{(-1)^{i+1}(\xi_1)^i \cdot \gamma^{i+1} \cdot \pi^{(i+1) \cdot \Pi_{j=1}^{i} (i - 2l + 1)}}{(i + 1) \cdot (2j + 1) \cdot (2j + 1) \cdot (j + 1) \cdot \Pi_{j=1}^{i} p_i}$$

(7)

According to the above equation, the anodic limiting current $I_{d,RPV}$ at spherical electrodes depends on the ratio between the diffusion coefficients of the electroactive species ($\gamma = D_0/D_6$) as well as on the $\xi_1$ and $\xi_2$ parameters. Therefore, $I_{d,RPV}$ is sensitive to the diffusion coefficient of the species R, electrode radius and relation between the duration of the potential pulses.

- **Planar electrodes.** By making $r_0 \rightarrow \infty$ ($\xi_1 \rightarrow 0$ and $\xi_2 \rightarrow 0$) in Eq. (6) we obtain:

$$I_{d,RPV}^{\text{plane}} = I_{d1}(t_1 + t_2) - P_{d2}(t_2) \frac{nFAC_0\sqrt{D_0}}{\sqrt{\pi t_2}} (x - 1)$$

(8)

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

**Scheme 1.** Structures of the species under study and of all the anions and cations of RTILs employed.
Ultra microelectrodes. The limit of Eq. (4) when $E_2 \rightarrow +\infty$ $(K_2 \rightarrow +\infty)$ and $c_k = 0$ tends to:

$$I_{UPV} = \frac{nFAC_D}{\sqrt{\pi}} \left( \frac{1}{1 + K_2} \right) \left( 1 + \frac{\pi DR}{r_0} \right)$$

(9)

According to the above expressions, at planar electrodes the anodic limiting current is independent of the value of the diffusion coefficient of the reduced species. Moreover, as we deduced in previous papers for double potential step chronoamperometry [7], when ultramicroelectrodes are used the ratio $I_{RPV}/I_{DC}$ tends to be constant, so that the simultaneous determination of both anodic and cathodic limiting currents is possible. Nevertheless, as was deduced above, the influence of $D_k$ on the anodic limiting current depends on the size of the electrode radius and the diffusion of the limiting species. In this interval of electrode radius values where the anodic limiting current is independent of the diffusion coefficient, the ratio

$$I_{RPV} = \frac{nFAC_D}{\sqrt{\pi}} \left( \frac{K_2}{1 + K_2} \right) \left( 1 - \frac{\pi DR}{r_0} \right)$$

(11)

being the relation between both limiting currents:

$$I_{RPV} \text{cathodic limit} = \left( 1 + \frac{\pi DR}{r_0} \right) I_{RPV} \text{anodic limit}$$

(12)

From Eqs. (10) and (11) it is deduced that the techniques do not give rise to the same response at spherical electrode under the conditions above discussed $(t_1 \gg t_2)$.

Planar electrodes. From Eqs. (10) and (11) expressions for the planar case are obtained by making $r_0 \rightarrow \infty$:

$$I_{RPV} \text{plane limit} = \frac{nFAC_D}{\sqrt{\pi}} \left( \frac{1}{1 + K_2} \right) - \frac{nFAC_D}{\sqrt{\pi}} \left( \frac{1}{1 + e^{\pm \theta}} \right)$$

(13)

in such a way that both limiting currents are identical in absolute value:

$$I_{RPV} \text{cathodic limit} = -I_{RPV} \text{anodic limit}$$

(15)

Moreover, the responses corresponding to both techniques at planar electrodes are symmetrical with regard to the formal potential (see Fig. 3a), that is:

$$I_{RPV} \text{plane limit} (e^{\pm \theta}) = -I_{RPV} \text{plane limit} (e^{\pm \theta})$$

(16)

This relation between the responses is the same as that existing in NPV between an oxidation and a reduction process. Thus, the expression for RPV at planar electrodes is identical to that corresponding to an oxidation process for NPV. Therefore, it can be considered that both responses are electrochemically complementary, taking into account that one refers to the reduction of species $O$ (NPV) and the other one to its “hypothetical” oxidation (RPV).

- Ultramicroelectrodes. As mentioned above, a steady-state response is obtained when $r_0 \ll \sqrt{\pi DR} t_2$; $t_1 \equiv O. R$. Thus, under these extreme conditions, NPV and RPV techniques give rise to identical responses:

$$I_{RPV} \text{plane limit} = \frac{nFAC_D}{\sqrt{\pi}} \left( \frac{1}{1 + K_2} \right)$$

(17)

In Fig. 3 the above-mentioned comparison between NPV and RPV techniques $(t_1 \gg t_2)$ applied to the process: $O + ne^- \rightleftharpoons R$ is summarized, including on the top of the figure a scheme of the potential-time perturbations corresponding to both techniques [1]. From this figure we can observe that, although the forms of both responses are identical, for a given potential value the difference between the NPV and the RPV signals is greater when the electrode size increases. These responses behave in a contrary way, as a reduction in NPV and tending to an oxidation in RPV, when planar electrodes are considered since the steady state can never be reached under these conditions (Fig. 3a). On the contrary, at ultramicroelectrodes both responses tend to be superimposable due to the “loss of memory”, so that the response in RPV is practically only cathodic (Fig. 3c). For larger spherical electrodes, intermediate behaviour is observed (Fig. 3b).

Note that all the above discussion refers to a simple reversible $E$ process. When the reaction product is involved in any other process, as occurs for example in the case of an EC mechanism, at planar and spherical electrodes the RPV anodic current is strongly affected by
Fig. 2. RPV curves when only species \( O \) is initially present for three electrode sizes: planar electrode (a), spherical electrode with \( r_0 = 3 \times 10^{-3} \text{ cm} \) (b) and ultramicroelectrode \( (r_0 < 10^{-6} \text{ cm}) \) (c). Five \( \gamma \) values are considered: \( \gamma^2 = 1/10 \) (–––––), \( \gamma^2 = 1/3 \) (–––––), \( \gamma^2 = 1 \) (––––), \( \gamma^2 = 3 \) (–––) and \( \gamma^2 = 10 \) (–––––). \( E_1 = \infty \), \( t_1 = 1 \text{ s} \), \( t_2 = 0.05 \text{ s} \), \( c_0 = 1 \text{ mM} \), \( c_x = 0 \text{ mM} \), \( D_O = 10^{-7} \text{ cm}^2/\text{s} \).
the chemical kinetics, whereas the NPV limiting current remains unaffected and only a small shift of the voltammogram toward more positive potentials takes place. Therefore, RPV is a very useful tool for detecting complications coupled to the charge transfer reaction. Note that no differences are observed when ultramicroelectrodes are used because of the achievement of the steady state.

3.2. Both electroactive species present in bulk solution ($c_2, c_k \neq 0$)

The analytical solution presented (Eq. (2)) permits the analysis of the case in which both species are initially present in the medium.

Obviously, the cathodic limiting current \( \text{\textit{Ile}} \) is also given by Eq. (5), since this is insensitive to the diffusion coefficient and the initial concentration of species \( R \). On the other hand, for more positive \( E_2 \) values, and particularly under anodic limiting conditions, \( I_{\text{UME}} \) is highly affected by the initial presence of the reduced species (see Fig. 4).

3.2.1. Anodic limiting current, \( I_{\text{RPV}} \) ($E_2 \rightarrow -\infty, \; K_2 \rightarrow +\infty$)

Under anodic limit conditions it is fulfilled that \( Y_2 \rightarrow 0, \; Z_2 \rightarrow -1 \) and \( \Omega_2 \rightarrow 1/\gamma^2$: \(I_{\text{RPV}} = I_{\alpha}(t_1 + t_2) - \frac{F_2}{2} (t_2) [1 + \left( \frac{G_2}{\gamma} \cdot \frac{c_0}{c_2} \right) (1 + \frac{\xi_2}{\gamma} - (\gamma - 1) \cdot \frac{Y_2}{t_2} (t_2) \cdot \left\{ (1 + \frac{\xi_2}{\gamma}) [1 - F_2(\xi_1)] + \frac{\xi_1}{\sqrt{\pi}} |G_2(\alpha) - 1| + \frac{\xi_2}{2 \sqrt{\pi}} S(\xi_1, \alpha) \right\} ] (18)

- Planar electrodes:

\[
I_{\text{RPV}}^\text{plane} = \frac{F_2}{2} (t_1 + t_2) - \frac{F_2}{2} (t_2) \cdot \left( 1 + \frac{c_2}{c_0} \right)
\]

(19)

- Ultramicroelectrodes:

\[
I_{\text{RPV}}^\text{ultramicro} = \frac{nFAC_k}{r_0} D_k (20)
\]

According to the above equations, when \( c_2 \neq 0 \) the anodic limiting current \( I_{\text{RPV}} \) depends on species \( R \) diffusion coefficient for any electrode size, including planar electrodes and ultramicroelectrodes, contrary to what happens when species \( R \) is not present in bulk solution.

In Fig. 4 we have plotted RPV curves for five diffusion coefficient ratios \( (D_0/D_k) \) and three electrode sizes, taking into account that both electroactive species are initially present at the same concentration \( (c_0 = c_k) \). As we have previously deduced, we can observe that the anodic limiting current is sensitive to the \( D_k \) value for all the electrode radii; in general, \( I_{\text{RPV}} \) increases with \( D_k \), contrarily to the case at which species \( R \) is not in bulk solution, described in Section 3.1.

Note that a crossing between RPV curves corresponding to different \( D_k \) values appears. From the corresponding analytical equations we have characterised this crossing at planar electrodes and ultramicroelectrodes:

- Planar electrodes. From Eq. (3) it is obtained:

\[
E_{\text{crossing}}^\text{plane} = E_{c0} - RT/nF \ln \left( \frac{c_2}{c_k} \right)
\]

(22)

where the value of the crossing potential \( E_c \) coincides with the null current or the equilibrium potential value calculated when
Fig. 4. RPV curves when both species are initially present for three electrode sizes: planar electrode (a), spherical electrode with $r_0 = 3 \times 10^{-5}$ cm (b) and ultramicroelectrode ($r_0 < 10^{-5}$ cm) (c). $\gamma^2 = 1/10$ (---), $\gamma^2 = 1/3$ (---), $\gamma^2 = 1$ (---), $\gamma^2 = 3$ (---) and $\gamma^2 = 10$ (---). $c_0 = c_1 = 1$ mM. Other conditions as in Fig. 2.
NPV is used. However, unlike NPV, in RPV technique this potential is not a null current or an equilibrium potential.

- Ultramicroelectodes: In this case, as was explained in Section 3.1.3, the responses of NPV and RPV techniques coincide and therefore,

$$I_{\text{UME}}^\text{crossing} = 0$$

(23)

$$E_{\text{UME}}^\text{crossing} = E_c^\circ + \frac{RT}{nF} \ln \left( \frac{c_0}{c_k} \right)$$

(24)

4. RPV experiments with Hg microelectrodes

From the above it may be inferred that RPV can be very useful for the determination of both diffusion coefficients and the formal potential of a redox couple from a single RPV experiment if the appropriate values for the electrode radius and pulses durations are selected. Thus, the diffusion coefficient of species O is immediately obtained from the value of the cathodic limiting current ($I_{\text{LDC}}$) and once $D_O$ is known, the diffusion coefficient of the reduced species can be determined from the anodic limiting current ($I_{\text{LPV}}$) by single-parameter fit of the analytical [Eq. (6)] and the experimental values. Finally, from the position in the potential axis of the RPV curve, the value of the formal potential is also available.

The difficulties of preparing solutions of known bulk concentration in ionic liquids required the accurate determination of the initial concentration of the oxidized species ($c_0^\circ$) from single potential step chronoamperometry [10]. For each case, $c_0^\circ$ value was determined under cathodic limiting conditions by the fit of the experimental current–time curves according to the equation below:
Table 2
Diffusion coefficients in the literature.

<table>
<thead>
<tr>
<th>Redox Couple</th>
<th>Medium</th>
<th>(D_0_\text{cm}^2s^{-1})</th>
<th>(D_0/D_0)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ru(NH₃)₆]³⁺/²⁺</td>
<td>0.1 M KX (^a)</td>
<td>6.7 (\times) 10⁻⁶</td>
<td>-</td>
<td>[13,17,18]</td>
</tr>
<tr>
<td>[CoSep]³⁺/²⁺</td>
<td>0.1 M NaClO₄</td>
<td>6.7 (\times) 10⁻⁶</td>
<td>-</td>
<td>[20,21]</td>
</tr>
<tr>
<td>[Co(C₅H₅)₂]³⁺/²⁺</td>
<td>[C₄ mim][BF₄]</td>
<td>3.16 (\times) 10⁻⁷</td>
<td>1.29</td>
<td>[10]</td>
</tr>
<tr>
<td>[Co(C₅H₅)₂]³⁺/²⁺</td>
<td>[C₂ mim][NTf₂]</td>
<td>1.11 (\times) 10⁻⁷</td>
<td>1.35</td>
<td>[10]</td>
</tr>
<tr>
<td>[Co(C₅H₅)₂]³⁺/²⁺</td>
<td>[C₄ mim][PF₆]</td>
<td>4.7 (\times) 10⁻⁷</td>
<td>1.65</td>
<td>[10]</td>
</tr>
</tbody>
</table>

\(^a\) Value for \(D_0\) in 0.1 M KNO₃.
\(^b\) Value for \(D_0\) in 0.1 M KCl.

\(I_d(t) = \frac{nFAc_iD_0}{r_0} + \frac{nFAc_i\sqrt{D_0}}{\sqrt{\pi t}}\) (25)

where \(A = 2\pi r_0^2\). The experimental value obtained for the second term of expression (25) (the planar contribution) was used in each case to normalize \(I_d(t)\) values for the determination of diffusion coefficients since it is observed that this normalization gives rise to a greater tolerance of \(I_{d,DC}\) and \(I_d(t)\) to the electrode radius uncertainty.

Room Temperature Ionic Liquids constitute an important field of application of this double potential technique, since rather unequal diffusion coefficients of the electroactive species are encountered in this medium [8–11,19]. So, the experimental study of the reduction of the cobaltocenium ion (Cc⁺) in several RTILs was performed by means of RPV at hemispherical mercury electrodes. The reduction processes of ruthenium and cobalt complexes in aqueous solutions were also tackled.

The values of the electrode radius and the duration of the potential pulses were selected in order to give good sensitivity. Note that, as mentioned above, the optimal values of the electrode size in conventional solvents, i.e. water or acetonitrile, correspond to the range of common microelectrodes, whereas in ionic liquids the use of ultramicroelectrodes is required due to the smaller values of diffusion coefficients as a consequence of the often higher viscosity. Thus, for RPV experiments in ionic liquids and in aqueous solution mercury hemispherical electrodes of ca. 5 \(\mu m\) and 25 \(\mu m\) radius, respectively, were employed.

In Fig. 5 the experimental and the theoretical RPV curves with \(t_1/t_2 = 20\) for the different redox couples are plotted, showing in all the cases an excellent agreement which validates the theoretical results herein presented.

In Table 1 the data corresponding to the best fit of experimental and analytical results are summarized, being in reasonable agreement with those previously reported in the literature (Table 2). In ionic liquids, diffusion coefficients up to two orders of magnitude smaller than in aqueous solution are found. It is also worth highlighting the higher diffusivity in this medium of the uncharged species (cobaltocene), with respect to the charged one (cobaltocenium) which interacts more favourably with the RTIL ions [10]. These interactions are also likely to explain the high solubility of CcPF₆ in these solvents, so that very concentrated solutions (66.8–98.6 mM) were prepared, which permitted a faradaic signal with non-significant noise to be obtained despite the small values of the diffusion coefficients and of the electrode size.

5. Conclusions

From a rigorous analytical solution obtained for Reverse Pulse Voltammetry at spherical electrodes, the appropriate conditions for the simultaneous determination of both diffusion coefficients and the formal potential of the redox couple with a single RPV experiment are established.

The successful experimental application of RPV for this purpose in Room Temperature Ionic Liquids, as well as in aqueous solution, is reported by using mercury hemispherical electrodes.

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Appendix A

A.1. Parameters and functions

\(\zeta_1 = \frac{2\sqrt{D_0(t_1+t_2)}}{r_0}\) (A.1)  
Sphericity parameter corresponding to the total time

\(\zeta_2 = \frac{\sqrt{D_0} t_2}{r_0}\) (A.2)  
Sphericity parameter corresponding to the duration of the second pulse

\(\lambda = \sqrt{\frac{r_0^2}{t_1+t_2}}\) (A.3)  
Square root of the ratio of the duration of the second pulse and of the total time

\(\gamma = \frac{D_0}{\lambda^2}\) (A.4)  
Square root of the ratio of the diffusion coefficients of the electroactive species

\(\eta_2 = \frac{p}{D_0}(E_2 - E')\) (A.5)  
Dimensionless potential of the second pulse

\(\Delta_2 = \exp(\eta_2)\) (A.6)  
\(\Delta_2 = \frac{1+\Delta_2}{1+\Delta_2}\) (A.7)  
\(J_2 = \frac{1+\Delta_2}{1+\Delta_2}\) (A.8)  
\(Z_2 = \frac{-\Delta_2}{\sqrt{\pi t_2}}\) (A.9)  
\(Y_2 = \frac{\lambda \eta_2 \Delta_2}{\Delta_2 + 1}\) (A.10)

\(p_{d,1}(t_1 + t_2) = \frac{nFAc_i \sqrt{D_0}}{\sqrt{\pi t_1 + t_2}}\) (A.11)  
\(p_{d,2}(t_2) = \frac{nFAc_i \sqrt{D_0}}{\sqrt{\pi t_2}}\) (A.12)  
\(I_{d,1}(t_1 + t_2) = \frac{p_{d,1}(t_1 + t_2)}{1 + \sqrt{\frac{D_0(t_1 + t_2)}}{r_0}}\) (A.13)

A.2. Series

Koutecký’s Function : \(F(x) = e^{x/2} \cdot \text{erfc}(x/2)\) (A.14)

being \(\text{erfc}\) the complementary error function.

\(G(x) = x \cdot \arcsin(x) + \sqrt{1-x^2}\) (A.15)

\(S^{\text{ser}}(\alpha,\zeta_1) = \sum_{n=2}^{\infty} \left\{ -\frac{1}{n-1} \cdot \left(\frac{\zeta_1}{\alpha}\right)^n \cdot \frac{\alpha^n}{\prod_{i=1}^{n-1} \beta_i} \cdot A \right\} (A.16)

\(\text{being :}\)

if \(2j < i\) : \(A = \frac{1}{2 j} \cdot \left(\frac{1}{2 j} - 1\right)^{j-i} \left(\frac{1}{2 j} - 1\right)^{i-j} \)
if \( 2j = i \):
\[
A = \sum_{i=0}^{j-1} \left[ (-1)^i \cdot \left( \frac{1}{2j} \right)^{2i} \cdot \frac{(j-i)!}{\Gamma(j-i)!} \right] + \frac{1 + (\gamma / \gamma' \cdot C_0)}{2^{2j-i}} \sum_{i=0}^{j-1} p_i \left( \frac{1}{2j} \right)^{2j-i-1}
\]
(A.17)
where the sum is only effective for \( j \geq 2 \)

if \( 2j > i \):
\[
B = \frac{1}{(2j+1) \cdot 2^j \cdot (j+1)!} \sum_{m=0}^{m=0} \left\{ (-1)^m \cdot 2^m \cdot \left[ \frac{1}{2j} \right]^{2m-1} \cdot \prod_{k=0}^{k=0} \left( \frac{j-k+1}{2k-1} \right) \right\}
\]

if \( 2j + 1 = i \):
\[
B = \frac{1}{(2j+1) \cdot 2^j} \sum_{m=0}^{m=0} \left\{ (-1)^m \cdot 2^m \cdot \left[ \frac{1}{2j} \right]^{2m-1} \cdot \prod_{k=0}^{k=0} \left( \frac{j-k+1}{2k-1} \right) \right\} + \frac{Y_z}{2} \left\{ 1 + (\gamma / \gamma' \cdot C_0) \right\} \cdot \frac{(-1)^i}{(i+1) \prod_{i=1}^{i=1} p_i} \left( \frac{1}{2j} \right)^{2j-1} \cdot \left( \frac{\gamma}{\gamma'} \right)
\]
where the sum is only effective for \( j \geq 1 \).

\[
\begin{align*}
\text{if even} : & \quad B = \frac{1}{(2j+1) \cdot 2^j \cdot (j+1)!} \sum_{m=0}^{m=0} \left\{ (-1)^m \cdot 2^m \cdot \left[ \frac{1}{2j} \right]^{2m-1} \cdot \prod_{k=0}^{k=0} \left( \frac{j-k+1}{2k-1} \right) \right\} \\
\text{if odd} : & \quad B = 0
\end{align*}
\]
(A.19)

References


