DC POLAROGRAPHY

CURRENT–POTENTIAL CURVES WITH AN EE MECHANISM

J. GALVEZ, R. SAURA, A. MOLINA and T. FUENTE
Laboratory of Physical Chemistry, Faculty of Science, Murcia (Spain)
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ABSTRACT

The dc polarographic response for the EE mechanism both in the expanding plane electrode and in the expanding sphere electrode is examined. Explicit equations for the current–potential curves when all species are initially added to the solution and without using the steady-state approximation have been derived. The situation obtained in some particular cases (reversible steps, one reversible and the other irreversible, totally irreversible steps and well-separated steps) is also discussed.

INTRODUCTION

The theory concerning multi-electron polarographic processes has received great attention in the literature, and therefore theoretical predictions based on the stationary plane electrode (SP), the expanding plane electrode (EP) and the more rigorous expanding sphere electrode (ES) have been examined [1 and refs. therein, 2–6]. However, Ružić [1] has suggested that the solution obtained for the EE mechanism with the EP model presents some difficulties because that solution is not always convergent. (In turn, Lovrić [6] has recently derived the solution for the EEE mechanism by adopting the EP model, although no analysis of this solution was made.)

The aim of the present paper is to show that the solutions obtained for the EE mechanism based both on the EP and on the ES model may be applied to the data analysis of the current–potential curves. In addition, these solutions are not limited to the case where only the oxidized form is present in the solution, so that under these conditions the quantitative kinetic data are simplified.

NOTATION AND DEFINITIONS

\[ r_0 = \text{electrode radius at time } t \]
\[ q = \text{electrode area} \]
$k_{f,j}, k_{b,j} =$ heterogeneous rate constants of the forward and reverse charge-transfer reactions of step $j$

$k_{s,j} =$ standard rate constant of step $j$

$K_j = k_{b,j}/k_{f,j}$

$i_{p} =$ total current in the EP model

$i_{p,j} =$ current of step $j$ in the EP model

$i_{d,a}(n_{j}) =$ diffusion current involving $n_{j}$ electrons in the EP model

$i_{p,j} = i_{p}/i_{d,a}(n_{j})$

$i_{p} =$ current in the ES model, the same meanings as the corresponding symbols in the EP model.

$\Gamma =$ Euler gamma function

$F(X) =$ Koutecky function [7] of argument $X$ in the EP model

$Fe(X) =$ Koutecky function of argument $X$ in the ES model

$k_{f}, k_{b} =$ heterogeneous rate constants of the forward and reverse charge-transfer reactions of the overall process ($A + ne^- \rightarrow C$)

$k_{s} =$ standard rate constant of the overall process

$K =$ $k_{b}/k_{f}$

\[ \frac{i_{d,a}(n_{j})}{n_{j}Fq} = k_{f,j}c_{A}(0,t) - k_{b,j}c_{C}(0,t) \]  

with the variables

\[ s_{t} = \sqrt{\frac{7/12D_{f}}{(r - n_{j})}} \]

\[ \xi_{t} = \frac{\sqrt{12D_{f}/7y^{2}1/6}}{t/6} \]

\[ \chi_{t} = \sqrt{\frac{12r}{7}\left(\frac{k_{f}}{D_{f}^{1/2}} + k_{b}/D_{b}^{1/2}\right)} \]

and expanding $c_{A}, c_{B}$ and $c_{C}$ as

\[ c_{A} = \sum c_{i,j}(s_{A})\xi_{i}^{j}X_{i} \]

\[ c_{B} = \sum c_{i,j}(s_{B})\xi_{i}^{j}X_{i} \]

\[ c_{C} = \sum c_{i,j}(s_{C})\xi_{i}^{j}X_{i} \]

allows one to reformulate the bvp as follows:

\[ \rho_{i,j}^{u}(s_{A}) + 2s_{x}\rho_{i,j}^{u}(s_{A}) - \frac{1}{2}(i + 3)\theta_{i,j}(s_{A}) \]

\[ = -\sum_{k=0}^{i-1}e_{k}\delta_{i-k-1,j}(s_{A}) \]

\[ \phi_{i,j}^{u}(s_{B}) + 2s_{x}\phi_{i,j}^{u}(s_{B}) - \frac{1}{2}(i + 3)\theta_{i,j}(s_{B}) \]

\[ = -\sum_{k=0}^{i-1}e_{k}\delta_{i-k-1,j}(s_{B}) \]

\[ \delta_{i,j}^{u}(s_{C}) + 2s_{x}\delta_{i,j}^{u}(s_{C}) - \frac{1}{2}(i + 3)\delta_{i,j}(s_{C}) \]

\[ = -\sum_{k=0}^{i-1}e_{k}\delta_{i-k-1,j}(s_{C}) \]

where

\[ e_{k}(s_{t}) = 2(-1)^{k}s_{t}^{k}\left\{ 1 - \frac{1}{2}(k + 3)s_{t}^{2}\right\} \]

$s_{t} \rightarrow \infty$:

\[ \rho_{i,j}^{u}(s_{B}) = c_{i}^{u}; \quad \phi_{i,j}^{u}(s_{B}) = c_{i}^{u}; \quad \delta_{i,j}^{u} = c_{i}^{u} \]

and $\theta_{i,j}, \phi_{i,j}, \delta_{i,j} \rightarrow 0$ unless $i = j = 0$

$s_{t} = 0$:

\[ \left( \frac{\partial c_{B}}{\partial s_{t}} \right) = -\gamma_{i}\left( \frac{\partial c_{A}}{\partial s_{t}} \right) - \gamma_{s}\left( \frac{\partial c_{C}}{\partial s_{t}} \right) \]
\[
\begin{align*}
\left( \frac{\partial c_A}{\partial s_A} \right) &= \frac{x_1}{1 + \gamma_1 K_1} \{ c_A(0, x_1) - K_1 c_B(0, x_1) \} \\
\left( \frac{\partial c_L}{\partial x_L} \right) &= \frac{\gamma_2 W x_1}{1 + \gamma_1 K_1} \{ c_B(0, x_1) - K_2 c_L(0, x_1) \}
\end{align*}
\]

and
\[
\gamma_1 = (D_{o_b}/D_{o_a})^{1/2}; \quad \gamma_2 = (D_{a_b}/D_{a_a})^{1/2}; \quad \gamma_3 = \gamma_1 / \gamma_2
\]
\[
W = k_{1,2}/k_{1,3} = (k_{1,2}/k_{1,3}) \exp(a_i J_i - a_j J_j)
\]
\[
J_i = (n_i F / RT)(E_i - E_i^0)
\]
\[
K_r = e^r
\]

We now can deduce from eqns. (11)–(17) by using conventional methods [8–11] an equation for the current in both electrode models (EP and ES).

**Expanding plane electrode**

Because the terms in \( \xi \) do not contribute to the current the system (11) must be solved for \( i = 0 \) only. By following the same derivational pattern mentioned above, we find
\[
\begin{align*}
\rho_{0,j}(s_A) &= a_j \Psi_{j+1}(s_A), \quad j > 0; \quad \rho_{0,0} = a_0 \Psi_0(s_A) + c_A^* \text{erf}(s_A) \\
\phi_{0,j}(s_B) &= b_j \Psi_{j+1}(s_B), \quad j > 0; \quad \phi_{0,0} = b_0 \Psi_0(s_B) + c_B^* \text{erf}(s_B) \\
\delta_{0,j}(s_C) &= c_j \Psi_{j+1}(s_C), \quad j > 0; \quad \delta_{0,0} = c_0 \Psi_0(s_C) + c_C^* \text{erf}(s_C)
\end{align*}
\]

Inserting eqns. (22) into eqns. (15)–(17) it follows that
\[
\begin{align*}
a_0 &= c_A^*; \quad b_0 = c_B^*; \quad c_0 = c_C^* \\
a_1 &= -\frac{1}{(1 + \gamma_1 K_1) \Psi_1}(c_A^* - K_1 c_B^*) \\
c_1 &= \frac{\gamma_2 W}{(1 + \gamma_1 K_1) \Psi_1}(c_B^* - K_2 c_C^*) \\
-a_j p_{j+1} x_j + a_j p_{j+1} y_j &= X_j a_j p_{j+1} / (1 + \gamma_1 K_1); \quad j \geq 2 \\
-c_j p_{j+1} x_j + c_j p_{j+1} y_j &= X_j c_j p_{j+1} / (1 + \gamma_1 K_1); \quad j \geq 2
\end{align*}
\]

where
\[
p_j = \frac{2 \Gamma(1 + j/2)}{\Gamma(1 + j/2)}
\]

\[
\frac{X_2}{1 + \gamma_1 K_1} \left[ \frac{\gamma_2 W (\gamma_2 + K_2) / (1 + \gamma_1 K_1) \Psi_1}{1 + \gamma_1 K_1} \right]
\]

In addition, if we make
\[
I_{1,p} = i_{d,p}(n_1); \quad I_{2,p} = i_{d,p}(n_2); \quad I_p = i_{d,p}(n_1 + n_2)
\]

where
\[
i_{d,p}(n) = n F q / (D_{o_b} / 3 \pi c_T)
\]

one obtains
\[
I_p = (n_1 I_1 + n_2 I_2) / (n_1 + n_2)
\]

Finally, combining eqns. (3), (5), (10), (22)–(27) yields the following expressions for \( I_{1,p} \) and \( I_{2,p} \):
\[
I_{1,p} = S_{1,p} / (1 + \gamma_1 K_1); \quad S_{1,p} = \sum_{j=1}^n \epsilon_j X_j
\]
\[
\epsilon_j = (-1)^{j} \epsilon_j / \prod_{i=0}^{j-1} p_{j+1}
\]
\[
\epsilon_j' = X_j \epsilon_{j-1} - X_j' \epsilon_{j-2}; \quad j \geq 3
\]
\[
\epsilon_j = A_1 - A_2 K_1
\]
\[
\epsilon_j' = A_1 - \frac{(1 + \gamma_1 K_1 + \gamma_2 W K_1) / (1 + \gamma_1 K_1) A_1 + \gamma_1 K_1 K_2 W A_2}{(1 + \gamma_1 K_1) A_2 + \gamma_1 K_1 K_2 W A_3}
\]
\[
A_1 = c_A^* / c_T; \quad A_2 = c_B^* / c_T; \quad A_3 = c_C^* / c_T
\]
\[
A_1 + A_2 + A_3 = 1
\]
\[
I_{2,p} = S_{2,p} / (1 + \gamma_1 K_2); \quad S_{2,p} = \sum_{j=1}^n \eta_j X_j
\]
\[
X_j = \sqrt{2 \pi / \gamma_1 K_1} \left[ (k_{1,2}/D_{1,2}^2 + k_{1,2}/D_{1,2}^2)^{1/2} \right]
\]
\[
\nu_j = (-1)^{j} \nu_j / \prod_{i=0}^{j-1} p_{j+1}
\]
\[
\nu_j' = Y_j \nu_{j-1} - Y_j \nu_{j-2}; \quad j \geq 3
\]
\[
\nu_j = - (A_2 - A_3 K_2)
\]
\[
\nu_j' = A_3 - \left[ K_2 \left( \gamma_1 K_2 W \right) A_2 + \gamma_1 K_2 W A_3 \right] / (1 + \gamma_1 K_2 W)
\]
with
\[ \gamma_0 = 1/\rho \]
\[ Y' = 1 + \frac{1 + \gamma_1 K_1}{\gamma_1 W(1 + \gamma_4 K_2)} \]
\[ Y_2 = \frac{1 + \gamma_1 K_2 + \gamma_1 \gamma_4 K_1 K_2}{\gamma_1 W(1 + \gamma_4 K_2)^2} \]  

(41)

In eqn. (36) the presence of \( \gamma_1 \) is due to the definition given for \( I_{2,p} \) (see eqns. 30 and 31).

On the other hand, although the power series in eqns. (33) and (36) are unconditionally convergent for all values of \( \chi_1 \) and \( \chi_2 \) (see Appendix A), convergence is slow when the arguments are greater than unity. Under these conditions it is useful to employ an asymptotic solution of eqns. (33) and (36). This is accomplished by expanding \( c_A, c_B \) and \( c_C \) in eqns. (10) as powers of \( \chi_i^{-1} \) and proceeding as previously. Therefore, we obtain

\[ I_{1,p} = \frac{(\gamma_1 + K_2)A_1 - (A_2 + \gamma_2 A_3)K_1 K_2 S_{2,p}}{\gamma_1 + K_2 + \gamma_1 \gamma_4 K_1 K_2} \]
\[ S_{2,p} = 1 + \sum_{j=1}^{\infty} E_{1,j} \chi_i^{-j} \]  

(42)

\[ E_{2,j} = \frac{Y_j p_{-3/7} E_{2,j-1} + Y_4 p_{-3/7} p_{-3/7} E_{1,j-2}}{1 + \gamma_1 K_1} \]  

(43)

\[ E_{1,1} = \frac{p_{-3/7} p_{-3/7} p_{-3/7} p_{-3/7} p_{-3/7} p_{-3/7} (1 + \gamma_1 K_1)}{\gamma_1 + K_2 + \gamma_1 \gamma_4 K_1 K_2} \left[ \frac{1}{\gamma_1 W(\gamma_1 + K_2)} \right] \]

\[ E_{1,2} = \frac{Y_j p_{-3/7} p_{-3/7} p_{-3/7} p_{-3/7} p_{-3/7} p_{-3/7} (1 + \gamma_1 K_1)}{\gamma_1 + K_2 + \gamma_1 \gamma_4 K_1 K_2} \left[ \frac{1}{\gamma_1 W(\gamma_1 + K_2)} \right] \]

\[ E_{1,3} = \frac{Y_j p_{-3/7} p_{-3/7} p_{-3/7} p_{-3/7} p_{-3/7} p_{-3/7} (1 + \gamma_1 K_1)}{\gamma_1 + K_2 + \gamma_1 \gamma_4 K_1 K_2} \left[ \frac{1}{\gamma_1 W(\gamma_1 + K_2)} \right] \]

Equations (33) and (36), together with the corresponding asymptotic solutions (eqns. 42 and 44), describe completely the problem in the context of the EP.

Equations (33), (36), (42) and (44) include a number of special cases of interest. These are as follows:

(a) Both steps are reversible (RR). Under these conditions \( k_{3,1} \) and \( k_{3,2} \gg 1 \) and from eqns. (42) and (44) we obtain

\[ I_{1,p} = \frac{(\gamma_1 + K_2)A_1 - (A_2 + \gamma_2 A_3)K_1 K_2}{\gamma_1 + K_2 + \gamma_1 \gamma_4 K_1 K_2} \]  

(46)

\[ I_{2,p} = \frac{Y_j p_{-3/7} p_{-3/7} p_{-3/7} p_{-3/7} p_{-3/7} p_{-3/7} (1 + \gamma_1 K_1) K_1 K_2}{\gamma_1 + K_2 + \gamma_1 \gamma_4 K_1 K_2} \]  

(47)

When \( A_2 = A_3 = 0, A_1 = 1 \) (only species A is initially added to the solution) and \( \gamma_1 = \gamma_2 = \gamma_1 = 1 \), eqns. (46) and (47) become coincident with those previously derived by Ružič [1].

(b) The first step is reversible (RI). In this case the boundary condition defined by eqn. (6) is simplified to

\[ c_A(0, t) = K_1 c_B(0, t) \]  

(48)
By using eqn. (48) instead of eqn. (6) and proceeding as previously we find

\[ I_{1,p} = \frac{A_1 - K_1 A_2}{1 + \gamma_1 K_1} + \frac{K_1}{1 + \gamma_4 K_2 + \gamma_4 K_4 K_2} \left( \frac{\gamma_1 A_1 + A_2}{1 + \gamma_1 K_1} - A_3 K_3 \right) \left( \chi'_2 \right) \]  

(49)

\[ I_{2,p} = \frac{1 + \gamma_1 K_1}{1 + \gamma_4 K_2 + \gamma_4 K_4 K_2} \left( \frac{\gamma_1 A_1 + A_2}{1 + \gamma_1 K_1} - A_3 K_3 \right) \left( \chi'_2 \right) \]  

(50)

where the argument, \( \chi'_2 \), of the Koutecký function is given by

\[ \chi'_2 = \frac{1 + \gamma_4 K_2 + \gamma_4 K_4 K_2}{1 + \gamma_1 K_1} \sqrt{\frac{12t}{7D_0}} k_{1,2} \]  

(51)

(c) The second step is reversible (IR). We now have

\[ I_{1,p} = \frac{1 + \gamma_4 K_2}{1 + \gamma_4 K_2 + \gamma_4 K_4 K_2} \left( A_1 - \frac{(\gamma_4 A_2 + A_3) K_1 K_2}{1 + \gamma_4 K_2} \right) \left( \chi'_1 \right) \]  

\[ I_{2,p} = \frac{A_2 - A_3 K_3}{\gamma_1 (1 + \gamma_4 K_2)} \]  

(52)

\[ + \frac{1}{1 + \gamma_4 K_2 + \gamma_4 K_4 K_2} \left( A_1 - \frac{(\gamma_4 A_2 + A_3) K_1 K_2}{1 + \gamma_4 K_2} \right) \left( \chi'_1 \right) \]  

\[ \chi'_1 = \frac{1 + \gamma_4 K_2 + \gamma_4 K_4 K_2}{1 + \gamma_4 K_2} \sqrt{\frac{12t}{7D_0}} k_{1,1} \]  

(d) Both steps are totally irreversible (t-I). Under these conditions we have:

\[ k_{1,1} = k_{1,2} = 0 \]

and from eqn. (29) one obtains

\[ X_1 - X_2 = 1 \]  

(53)

Inserting this equation in eqns. (34) it follows (for \( A_i = 1 \)) that \( \epsilon'_j = 1 \) whatever \( j \). Accordingly, eqn. (33) becomes

\[ I_{1,p} = F \left( \left( 12t/7D_0 \right)^{1/2} k_{1,1} \right) \]  

(54)

In turn, for the second step it follows from eqns. (41) that

\[ Y_1 - Y_2 = 1 \]  

(55)

Introducing this condition in eqns. (38) and (39) one finds (see Appendix B) that \( I_{2,p} \) is given by

\[ I_{2,p} = F \left( \left( 12t/7D_0 \right)^{1/2} k_{1,2} \right) - \gamma_1 W F \left( \left( 12t/7D_0 \right)^{1/2} k_{1,3} \right) \]  

\[ 1 - \gamma_1 W^{\chi'_2} \]  

(56)

(e) Well-separated steps. In this case \( \Delta E = E'_2 - E'_1 < 0 \), \( W < 1 \) and from eqns. (29) and (41) one obtains (\( A_i = 1 \))

\[ X'_1 - X'_2 \approx 1; \quad Y'_1 - Y'_2 \approx 1 \]

Using these relationships and proceeding as in (d) we have

\[ I_{1,p} = \left( 1 + \gamma_1 K_1 \right)^{-1} F \left( \chi'_1 \right) \]  

(57)

\[ I_{2,p} = \frac{1}{1 + \gamma_4 K_2 + \gamma_4 K_4 K_2} \left( \frac{F \left( \chi'_1 \right) - F \left( \chi'_{2} \right)}{Y'_2} \right) \]  

(58)

At potentials increasing in the cathodic direction on the plateau of the first wave we have \( K_1 = 0, Y_2 = 1 \), and eqn. (58) is simplified to

\[ I_{2,p} = \left( 1 + \gamma_4 K_2 \right)^{-1} F \left( \chi'_2 \right) \]  

(59)

i.e. under these conditions both steps may be considered as independent [deviations between eqns. (58) and (59) become greater as \( \Delta E \) increases].

Expanding sphere electrode

For simplicity we shall consider that \( \gamma_1 = \gamma_2 = \gamma_3 = 1 \). In addition, in this section we show only the following particular cases (the general solution is given in Appendix C).

(a) RR. In this case, it is readily shown (see Appendix C) that \( I_{1,p} \) (\( j = 1, 2 \)) is given by the same expressions as \( I_{1,p} \) (eqns. 46 and 47). This situation is analogous to that previously reported by Ružičić [1] for the SP and EP models. Note, however, that \( i_{1,p} \neq i_{1,s} \) because \( i_{1,p} \neq i_{2,p} \).

(b) RI. When the first step is reversible we find that \( I_{1,p} \) is also defined by the same equations as \( I_{1,p} \) (eqns. 49 and 50) if in these equations we replace \( F \left( \chi'_2 \right) \) with \( F \left( \chi'_2 \right) \), where

\[ F \left( \chi'_2 \right) = \left( F \left( \chi'_2 \right) + \xi T \right) \left( 1 + \theta \xi \right) \]  

(60)

\[ T = \sum_{j=2} F_j \chi'_j \]  

(61)

\[ F_j = \left( \frac{(-1)^j u_{j-1} - F_{j-1}}{\prod_{i=0}^{j-1} \rho_{3j-2i-1}; j \geq 2} \right) / \rho_{3j-2i-1} \]  

(62)

\[ F_i = 0 \]

being \( u_{j} \) defined by eqn. (C.4). For values of \( \chi'_2 \approx 1 \) an asymptotic solution for the power series exists. This is given in Appendix C.

(c) IR. As we have seen in (b), \( I_{1,s} \) is also obtained by substituting \( F \left( \chi'_2 \right) \) with \( F \left( \chi'_2 \right) \) in eqns. (52).

RESULTS AND DISCUSSION

For simplicity we shall limit our discussion to the cases \( n_1 = n_2 = 1 \) and \( \gamma_1 = \gamma_2 = \gamma_3 = 1 \). In addition we may distinguish three cases.
(1) Well-separated steps. In this case we have $\Delta E < 0$ and one obtains totally resolved waves. Under these conditions current–potential (I/E) curves can be obtained from eqns. (57) and (58), and therefore Fig.1 shows I/E curves for different values of $\Delta E$ [deviations with rigorous eqns. (33) and (36) are negligible]. Note that the separation between the waves becomes smaller as $\Delta E$ increases. On the other hand, in order to consider both steps as independent $\Delta E$ must be $\leq -0.2$ V. Thus, for $\Delta E = -0.2$ V deviations between eqns. (58) and (59) are about 10% and they increase with $\Delta E$ (if $\Delta E = -0.1$ V, the error introduced by eqn. 59 is $\approx 30\%$).

In turn, in Figs. 2 and 3 we show the dependence of the I/E curves on $A_j$ for the IR and RI cases. These curves are appropriate in order to determine $E_i^0, \alpha_i$, and $k_{s,i}$. Thus, if $I_j(A_j)$ ($j = 1$ or 2; $j = 2$ or 3) is the I$_j$-value for a given value of $A_j$, it follows from eqns. (49)-(52) that for any value of $E$ we have

$$ I/R: A_2 = 0, \quad A_j = A_2 \quad (A_1 = 1 - A_2) $$

$$ K_1 = I_1(1)/(I_2(0) - I_1(0)) $$

$$ K_2 = (I_1(0) - I_2(0))/I_2(0) $$

$$ F(\chi_i^j) = I_1(0) - I_1(1) $$

Equations (63) allow us to calculate $E_i^0$ and $E_i^0$. In turn, from eqn. (64) we obtain $F(\chi_i^j)$ as a function of $E$, and also (with the aid of tabulated tables) $\chi_i^j$. This then allows us to determine $\alpha_i$ and $k_{s,i}$. If we make $A_2 = 0$, $A_j = A_3$, we find similar expressions to eqns. (63) and (64).

$$ R/I: A_2 = 0, \quad A_j = A_3 \quad (A_1 = 1 - A_3) $$

Fig. 1. Current–potential curves (eqns. 57 and 58) with $n_1 = n_2 = 1, T = 298$ K, $D_a = D_b = D_c = 10^{-3}$ cm$^2$ s$^{-1}, r = 3$ s, $E_i^0 = 0$ V, $k_{s,1} = k_{s,2} = 10^{-3}$ cm s$^{-1}, \Delta E$-values shown on the curves.

$$ K_1 = (1 - I_1(0))/(I_1(0) - I_2(0)) $$

$$ K_2 = I_2(0) - I_2(0)/I_2(0)(1 - I_2(0)) $$

$$ F(\chi_i^j) = I_2(0) - I_1(1) $$

As previously, these equations also allow $E_i^0, \alpha_i$, and $k_{s,i}$ to be calculated. However, in this case, from the dependence of $I_j$ on $A_2$ ($A_j = 0$) we cannot derive equations similar to expressions (65) and (66).

Figure 4 shows I/E curves when the waves are totally irreversible for several values of $\Delta E$. From eqns. (54) and (56) it follows that when $\Delta E < 0$ ($W < 1$), $I_{j,p}$ ($j = 1, 2$) is given by

$$ I_{j,p} = F((12/7D)^{1/2}k_{s,i}) $$

i.e. the curves obtained show the same behaviour as those involved with single-step processes discussed elsewhere [12-14]. One finds that totally irreversible waves are
obtained for values of $k_{eq} \leq 5 \times 10^{-3}$ cm s$^{-1}$ (deviations < 5%).

Figures 5 and 7 illustrate the effects of sphericity on the $I/E$ curves for cases IR and RI when the waves are not normalized [8] and for different values of $\Delta E$. Figures 6 and 8 show the results obtained when the curves are normalized. Note that the normalization of the waves strongly decreases the influence exerted by the curvature of electrode independently of the $\Delta E$ value (this situation is similar to that previously described for other mechanisms [8-10]). In any case, it is readily shown that if $\Delta E < 0$ the quantitative kinetic data analysis described above for the EP model is also valid if in eqns. (64) and (66) we replace $F(x_0')$ with $F(x_0')$.

(2) $I/E$ curves for the case $E_0' = E_3'$. In this section we consider the situation where the values of $E_0'$ are approximately comparable so that $\Delta E$ is within the
interval 0.1 $\gg$ $\Delta E$ $\gg$ 0.1 V. Under these conditions and if $A_t = 1$, one single wave is usually observed—or if the $k_{s_t}$ values are appropriate, incompletely resolved waves (see Figs. 1, 4, 5–8). In these cases, we may provide evidence that a stepwise process is operative from dependence of $I/E$ curves on the ratio $A_t/A_3$. Thus, for the overall process

$$A + 2 e^- \rightarrow C \quad \left[ E^0 = \frac{(E^0_1 + E^0_2)}{2} \right]$$

we have [7]

$$I_p = \frac{1 - (1 + K)A_3}{1 + \gamma_2 K} \left( \sqrt{\frac{12t}{7D_A}} k_t(1 + \gamma_2 K) \right)$$  \hspace{1cm} (68)

Hence, if we consider the $E$-value where $I_p = 0$ ("crossing potential", $E_c$) from eqn. (68) one obtains ($n = 2$

$$E_c = \frac{1}{2} \left( E^0_1 + E^0_2 \right) + \left( \frac{RT}{2F} \right) \ln \left( \frac{A_t}{A_3} \right)$$  \hspace{1cm} (69)

i.e. a plot of $E_c$ vs. $\ln(A_t/A_3)$ is linear with slope $RT/2F$ and intercept $(E^0_1 + E^0_2)/2$. Note that this plot is independent of the argument involved in eqn. (68), i.e. (69) remains valid for any value of $a$, $k_t$ and $t$.

Conversely, if the electrode process involves two steps, from the equations derived above it follows that a plot of $E_c$ vs. $\ln(A_t/A_3)$ cannot be linear and, in addition, it will show a dependence on the $a_t$, $k_{s_t}$ and $t$ values (in some cases this plot is approximately linear, although the slope and/or intercept values are different from those predicted by eqn. 69). Thus, in Fig. 9 we have plotted $I/E$ curves for $\Delta E = 0$ V, $t = 3$ s and different values of $A_t$ (rigorous solution). In Fig. 10 an analogous plot for $\Delta E = +0.1$ V is shown (IR solution). In turn, in Fig. 11 we have plotted the $E_c$-values vs. $\log(A_t/A_3)$ for $t = 3$ s (Figs. 9 and 10), as well as for $t = 1$ s.

In Fig. 11 the corresponding plots for the overall process are also included. Note that these curves allow us to discriminate if the electrode process involves two steps or, conversely, one single step is operative.

For $t_1$ processes one single wave is observed (Fig. 4). In the particular cases where $E^0_1 = E^0_2$, $k_{s_1} = k_{s_2}$ (i.e. $x_1 = x_2$) from eqns. (54) and (56) one obtains

$$I_p = F \left( \frac{(12t/7D_A)^{1/2}}{k_{s_1}} \right)$$

Hence, if the $I$-values are ascribed to a process involving one single multi-electron step the $a$ and $k_{s_t}$-values found are equal to $a_t n_z/n$ and $k_{s_t}$ respectively.

Finally, it is interesting to show that for $\Delta E = 0$ the $I$-values computed with eqns. (57) and (58) (which have been derived with the condition $\Delta E < 0$) show only small deviations with those obtained from rigorous equations for $k_{s_t}$-values $< 5 \times 10^{-3}$ cm$^{-1}$. In addition, there is a compensation between $I_1$ and $I_2$ so that the error introduced in the $I$-value by eqns. (57) and (58) is decreased (see Table 1). Accordingly, it follows that for both stable and moderately stable intermediates, eqns. (57) and (58) can be used for the quantitative kinetic data analysis.
(3) \( I/E \) curves when \( E^0_1 \ll E^0_2 \). This situation is the most difficult to analyse, and we find the following difficulties:

(a) In these cases it is often difficult to discriminate between a mechanism involving two steps and the overall process where a single multi-electron step is operative. Thus, the criteria exposed above for the \( \Delta E = 0 \) case are not valid because one finds that the corresponding plots are practically linear and, in addition, are in agreement with eqns. (69).

(b) The behaviour of the \( I/E \) curves depends to a large extent on the \( k_{-j} \) and \( \Delta E \)-values. Thus, for given values of \( k_{-j} \) the deviations between the \( I/E \) curves for a two-step mechanism and the corresponding curves for the overall process become larger as \( \Delta E \) increases. This is shown in Fig. 12 where we have plotted \( I \) vs. \( E \) for \( \Delta E = 0.4 \text{ V} \) and \( k_{-j} = k_{-j} = 1 \text{ cm s}^{-1} \). It is readily verified that this plot is almost coincident with the \( I/E \) curve for the irreversible process \( A + 2 e^- \rightleftharpoons C \) (\( E^0 = 0.2 \text{ V} \)). However, if \( \Delta E = 1 \text{ V} \), one finds that even for \( k_{-j} = 20 \text{ cm s}^{-1} \) the \( I/E \) curve for a two-step mechanism (Fig. 12) shows a behaviour which may be considered quasi-reversible if that curve is assigned to a process with a single, two-electron step (these results are in agreement with those previously obtained by Ružič et al. [1,2] from the ssa and by using digital simulation techniques).

In any case, a quantitative kinetic data analysis can be easily carried out for the IR, RI and \( tl \)-1 cases, proceeding as follows:

\[
I_p = (2 + K_j) F(\chi_i)/2(1 + K_j + K_i K_j) \tag{70}
\]

In addition it is readily shown that if \( \Delta E < 0 \) at potentials where the wave appears,
eqn. (70) is simplified to

$$I_p = F\left(\frac{(12t/7D\alpha)^{1/2}}{k_{11}}\right)$$  \hspace{1cm} (71)

i.e., under these conditions the I/E curves become independent of $\Delta E$ (see Figs. 5 and 7), and the $a_i$- and $k_{si}$-values can be obtained from established procedures [12–14]. However, if the $I$-values are ascribed to a single two-electron step rather than to a two-step mechanism it is readily shown [13,14] that the $a_i$- and $k_{si}$-values are

$$a_i = a_{1/2}$$

$$k_{si} = k_{si,1} \exp(-a_i F \Delta E / 2RT)$$  \hspace{1cm} (72)

Deviations between eqns. (70) and (71) (and therefore the validity of eqns. 72) increase as $\Delta E$ decreases. Thus, for $\Delta E = 0.1$ V and $\Delta E = 0.2$ V the error introduced by eqn. (71) is about 40% and 3% respectively, when $I \approx 0.1$ (deviations decrease as $I$ becomes greater).

(2) RI. In this case if $A_i = 1$ the current is given by

$$I_p = \frac{1}{1 + K_1} \left\{ 1 + \frac{2K_1 + 1}{1 + K_1 + K_1K_2} F(X_1) \right\}$$  \hspace{1cm} (73)

At potentials where the current magnitude becomes significant no simplification in eqn. (73) is possible. Hence, the procedure for calculation of $a_i$ and $k_{si,1}$ exposed above for case IR cannot be applied in these conditions.

However, if the I/E curves are obtained with the condition $A_i = 1$, eqn. (73) is now

$$I_p = -\frac{K_1(2K_1 + 1)}{2(1 + K_1 + K_1K_2)} F(X_2)$$  \hspace{1cm} (74)

At potentials where the anodic wave is operative, this equation becomes

$$I_p = -F(12t/7D)^{1/2} k_{b,2}$$  \hspace{1cm} (75)

Accordingly, the I/E curves also become independent of $\Delta E$ and one may determine $a_2$ and $k_{b,2}$ proceeding as previously for case IR. In turn, eqns. (72) are now

$$a_i = (1 - a_2)/2$$

$$k_{si,2} \exp(-(1 - a_2) F \Delta E / 2RT)$$  \hspace{1cm} (76)

(3) ti–tl. When $A_i = 1$ and $\Delta E > 0$ ($W > 1$, see eqn. 19) from eqns. (54) and (56) one obtains

$$I = F(12t/7D)^{1/2} k_{11}$$  \hspace{1cm} (77)

and therefore, all conclusions exposed above for case IR are also now valid.

APPENDIX A

In the power series defined by eqn. (33) we have

$$R^{-1} = \lim_{j \to \infty} \left| \frac{X_j X_{j+1}}{X_j}ight| = \lim_{j \to \infty} \left| \frac{p_j}{p_{j+1}} \right|$$  \hspace{1cm} (A1)

If $A_i = 1$, in eqns. (34) it holds that

$$\epsilon_1 = \epsilon_2 = 1$$  \hspace{1cm} (A2)

In addition, it is readily shown by induction

$$1 < \frac{\epsilon_j}{\epsilon_{j-1}} < X_j, \quad j \geq 3$$  \hspace{1cm} (A3)

In turn, for $j \geq 1$ we have [15]

$$p_{j+1} = (6j+1)(1+7/12j+...)$$  \hspace{1cm} (A4)

Introducing eqn. (A4) and the relationship (A3) in eqn. (A1) one obtains

$$R = +\infty$$  \hspace{1cm} (A5)

i.e. the radius of convergence of the power series defined by eqn. (33) is infinite, and therefore this series is unconditionally convergent for all values of $X_j$. Convergence of the power series given by eqn. (36) is seen in an analogous way.

APPENDIX B

If $A_i = 1$ and $Y_1 = 1$, from eqns. (38) and (39) one finds that $\nu_j$ is given by

$$\nu_j = \frac{1}{W} \sum_{i=0}^{j-1} Y_j = \frac{Y_{j-1}}{W(Y_j - 1)}, \quad j \geq 2$$  \hspace{1cm} (B1)

Introducing this equation in eqns. (36)–(39) (with $K_1 = K_2 = 0$) and taking into account that $F(X)$ is defined by [7]

$$F(X) = \sum_{j=1}^{\infty} \frac{(-1)^{j+1}X^j}{\sum_{j=0}^{\infty} p_j p_{j+1} \cdots p_{j+(j-1)/2}}$$  \hspace{1cm} (B2)

one may obtain, after some manipulations, eqn. (56).

APPENDIX C

**Expanding sphere electrode**

For simplicity we shall consider that $\gamma_1 = \gamma_2 = \gamma_3 = 1$. Under these conditions we have

$$I_{1,8} = \frac{1}{1 + K_1} \left\{ \frac{S_1 + \xi T_1}{1 + \theta \xi} \right\}$$  \hspace{1cm} (C1)
where

\[ T_i = \sum_{j=2}^{n} H_j x_j^i \]

\[ -H_{j+1} = \frac{u_j v_{j+1}}{p_{j+1}/7} \left( 1 - \frac{u_j v_{j+1}}{u_j p_{j-1}/7} x_j^i v_{j+1} \right) \]

\[ + x_j \frac{H_j}{p_{j+1}/7} + x_{j-1} \frac{H_{j-1}}{p_{j+1}/7} ; \quad j \geq 2 \]

\[ H_i = 0 \]

\[ H_2 = -\frac{u_2 v_2}{p_{2}/7} \]

\[ u_j = \frac{7}{44} (3j + 4) p_{j+1}/7 p_{j+1}/7 - 3j(3j + 8)/22 \]

\[ \theta = \frac{7}{11} p_{1}/7 (= 0.7868) \]

\[ I_{i, e} = \frac{1}{1 + \theta \xi} \left( S_{2, p} + \xi T_2^* \right) \]

\[ T_2 = \sum_{j=2}^{n} M_j x_j^2 \]

\[ M_{j+1} = \frac{u_j v_{j+1}}{p_{j+1}/7} \left( 1 - \frac{u_j v_{j+1}}{u_j p_{j-1}/7} x_j^i v_{j+1} \right) \]

\[ - y_j \frac{M_j}{p_{j+1}/7} - y_{j-1} \frac{M_{j-1}}{p_{j-1}/7} ; \quad j \geq 2 \]

\[ M_j = 0 \]

\[ M_2 = \frac{u_2 v_2}{p_{2}/7} \]

In turn, the corresponding asymptotic solution is given by

\[ I_{1, e} = \left( \frac{1 + K_2}{1 + K_2} A_1 - (A_3 + A_4) K_2 K_2 \right) S_{1, p} + \theta T_1^* \]

\[ T_1^* = \theta + \sum_{j=1}^{i} E_j^* x_j \]

\[ I_{2, e} = \left( \frac{1}{1 + K_1} A_2 - (1 + K_1) K_2 A_4 \right) S_{2, p} + \theta T_2^* \]

\[ T_2^* = \theta + \sum_{j=1}^{i} E_j^* x_j^4 \]

\[ E_{1, e} = \left( \frac{\theta p_{-2}/7 + v_1}{p_{-2}/7} e_{1, e} / p_{-2}/7 \right) \]

\[ E_{2, e} = \left( \frac{\theta p_{-2}/7 + v_1}{p_{-2}/7} e_{2, e} / p_{-2}/7 \right) \]

\[ E_{1,2} = \left( \frac{p_{-2}/7 (1 + K_2)}{1 + K_2} K_2 \right) \left( \frac{K_1}{K_1} \right) \]

\[ + E_{1,2} / p_{-2}/7 \]

\[ E_{2,2} = \left( \frac{p_{-2}/7 (1 + K_2)}{1 + K_2} K_2 \right) \left( \frac{K_1}{K_1} \right) \]

\[ + E_{2,2} / p_{-2}/7 \]

\[ E_{1, j} = \frac{E_{1, j}}{p_{-3j}/7} \]

\[ - x_j \frac{E_{1, j-1}}{p_{-3j}/7} - x_j \frac{E_{1, j-2}}{p_{-3j}/7} p_{-3j}/7 p_{-3j}/7 j \geq 3 \]

\[ E_{2, j} = \frac{E_{2, j}}{p_{-3j}/7} \]

\[ - y_j \frac{E_{2, j-1}}{p_{-3j}/7} - y_j \frac{E_{2, j-2}}{p_{-3j}/7} p_{-3j}/7 p_{-3j}/7 j \geq 3 \]

\[ v_j = - \left( \frac{3j(3j - 8)/22 + 7}{44} (3j - 4) p_{-3j}/7 p_{-3j}/7 \right) \]

\[ k = \frac{1 + K_1}{W(1 + K_2)} \]

If \( k_{\alpha, \beta} > 1 \), from eqns. (C1) and (C6) one obtains

\[ I_{j, e} = I_{j, p} \]

REFERENCES