THEORETICAL ANALYSIS OF CURRENT–POTENTIAL CURVES FOR THE CE AND EC MECHANISMS WITH NON-NERNSTIAN BEHAVIOUR

J. GALVEZ, R. SAURA and A. MOLINA
Laboratory of Physical Chemistry, Faculty of Science, Murcia (Spain)
(Received 13th September 1982)

ABSTRACT

The dc polarographic response for the CE and EC mechanisms with non-Nernstian behaviour is examined at an electrode expanding in accordance with any power law. Explicit equations for the current–potential curves which take into account the influences exerted by both the chemical reaction and the charge-transfer reaction have been derived in a rigorous way. An approach to quantitative kinetic data analysis is proposed.

INTRODUCTION

The equations used for electrode processes involving chemical reactions coupled to the charge-transfer step have been derived (both for the DME and in a stationary electrode) by using the steady-state approximation (ssa) [1–5], or when this approximation is avoided, by adopting Nernstian behaviour (Nb) [4–11]. Recently [12], the rigorous theory concerning a CE mechanism with non-Nernstian behaviour (nNb) has been derived without using the ssa. However, that solution depends on integral equations that must be solved by numerical methods. In turn, Galvez et al. have obtained explicit equations for the current–potential curves for different mechanisms [8–11], although in all these cases Nb was adopted. In any case, the equations found for both types of electrodes were normally obtained by following different procedures of derivation.

The aim of the present paper is to obtain explicit equations for the CE and EC mechanisms under nNb, which are valid for an electrode expanding in accordance with any power law. Thus, the equations used for a DME (expanding plane electrode model) or a stationary electrode result in only special cases of this general solution. In addition, an approach to quantitative kinetic data analysis in order to determine the rate constants, both of the chemical reaction and of the charge-transfer step, is also discussed.
NOTATION-DEFINITIONS

$k_1, k_2$ = rate constants for forward and reverse chemical reaction

$K$ = equilibrium constant for chemical reaction ($= k_1/k_2$)

$k_{1a}, k_{1b}$ = heterogeneous rate constants of the forward and reverse charge-transfer reaction

$k_{a}$ = $k_{a}/k_{1a}$

$\Gamma$ = Euler gamma function

$i$ = total d.c. faradaic current

$i_{1a}$ = total d.c. faradaic current under Nb

$i_{1c}$ = diffusion-controlled d.c. faradaic current

$i_{1d}$ = total cathodic limiting current

$i_{1d}$ = total anodic limiting current

$I$ = $i/i_{1d}$

$I_{1a} = i_{1a}/i_{1d}$

$I_{1c} = i_{1c}/i_{1d}$

Other notation/definitions are conventional.

THEORY

CE mechanism

The CE mechanism may be represented by

$$ B \text{C} + n e \rightarrow \text{D} $$

If the electrode area, $q(t)$, is given by the general law

$$ q(t) = q_0 e^{i} (z \gg 0) $$

and if $\delta_{z}$ is the operator,

$$ \delta_{z} = \left( \frac{1}{t} \frac{\partial}{\partial t} + \frac{z}{t} \frac{\partial}{\partial x} \right) $$

the boundary value problem (bvp) for mechanism (1) is given by

$$ \delta_{w} e_{n} = -k_{1} e_{m} + k_{2} e_{c} $$

$$ \delta_{z} e_{c} = k_{1} e_{m} - k_{2} e_{c} $$

$$ \delta_{1} e_{c} = 0 $$

$$ x = 0, z \gg 1 \quad e_{n} = e_{0}^{*}; \quad e_{c} = e_{c}^{*}; \quad e_{D} = e_{D}^{*} $$

$$ x > 0, z \to \infty \quad D_{1} \left( \frac{\partial e_{c}}{\partial x} \right) = -D_{2} \left( \frac{\partial e_{m}}{\partial x} \right) = i/nFq(t) $$

$$ D_{a} \left( \frac{\partial e_{a}}{\partial x} \right) = 0 $$

$$ c_{n} \frac{d^{2} [c_{n}]}{dx^{2}} + 2c_{n} \frac{d [c_{n}]}{dx} - 2w \frac{d [c_{n}]}{dx} = 0 $$

$$ \phi \frac{d^{2} [\phi]}{dx^{2}} + 2c_{D} \frac{d [\phi]}{dx} - 2w \frac{d [\phi]}{dx} = 0 $$

$$ \delta_{w} [c_{D}] = 0 $$

$$ \phi [s_{D}, x, w] = \sum_{j,m} \eta_{j,m} (s_{D}) \chi^{j} w^{m} $$

$$ c_{D} (s_{D}, x, w) = \sum_{j,m} \delta_{j,m} (s_{D}) \chi^{j} w^{m} $$

the bvp can be reformulated as follows:

$$ \frac{\partial c_{n}}{\partial x} (s_{c}) + 2c_{n} \frac{\partial c_{n}}{\partial x} (s_{c}) = \frac{2}{2z+1} (2j+m) s_{n} (s_{c}) = 0 $$

$$ \frac{\partial p_{j,m} (s_{c}) + 2c_{n} \frac{\partial p_{j,m} (s_{c})}{\partial x} = \frac{2}{2z+1} (2j+m) p_{j,m} (s_{c}) = 0 $$

$$ \eta_{j,m} (s_{D}) + 2s_{D} \eta_{j,m} (s_{D}) = \frac{2}{2z+1} (2j+m) \eta_{j,m} (s_{D}) = 0 $$

Introducing the new variables

$$ \tilde{s} = c_{0} + c_{c} $$

$$ \phi = (c_{n} - K c_{c}) \exp((k_{1} + k_{2}) t) $$

the assumption that

$$ D_{b} = D_{c} $$

and using the transformations

$$ s_{n} = \frac{2z+1}{4D_{f}} x $$

$$ x = (k_{1} + k_{2}) t $$

$$ w = \frac{4t}{2z+1} \left( \frac{k_{a}}{D_{a}^{1/2}} + \frac{k_{b}}{D_{b}^{1/2}} \right) $$

eqns. (1) are reduced to

$$ \frac{\partial^{2} c_{n}}{\partial x^{2}} + 2c_{n} \frac{\partial c_{n}}{\partial x} - 2w \frac{d [c_{n}]}{dx} = 0 $$

$$ \frac{\partial^{2} \phi}{\partial x^{2}} + 2c_{D} \frac{d [\phi]}{dx} - 2w \frac{d [\phi]}{dx} = 0 $$

$$ \frac{\partial c_{D}}{\partial x} + 2c_{D} \frac{d [c_{D}]}{dx} - 2w \frac{d [c_{D}]}{dx} = 0 $$

In addition, expanding $\tilde{x}$, $\phi$, and $c_{D}$ as

$$ \tilde{x} (s_{c}, x, w) = \sum_{j,m} \delta_{j,m} (s_{c}) \chi^{j} w^{m} $$

$$ \phi (s_{c}, x, w) = \sum_{j,m} \delta_{j,m} (s_{c}) \chi^{j} w^{m} $$

$$ c_{D} (s_{D}, x, w) = \sum_{j,m} \delta_{j,m} (s_{D}) \chi^{j} w^{m} $$

(1)
where
\[ s_j \rightarrow \infty : a_{0,0} = c_0^* + c_D^* (= 0^*); \quad p_{0,0} = 0; \quad \eta_{0,0} = c_D^* \]
(11)
\[ a_{j,m} \quad \text{and} \quad \eta_{j,m} \rightarrow 0 \quad \text{unless} \quad j = m = 0; \quad p_{j,m} \rightarrow 0, \quad j, m \geq 0 \]
(12)
\[ s_i \rightarrow 0: \]
(13)
(14)
(15)
with
\[ \gamma_1 = (D_c/D_0)^{1/2} \]
\[ K_1 = \exp(nF(E - E_0)/RT) \]
(16)
From eqns. (10)–(12) and by using conventional methods [8–10], we find
\[ a_{j,m} = a_{0,0} \Psi_{(2j+m)/(2z+1)}(x_c), \quad j, m \geq 0 \]
(17)
\[ a_{0,0} = a_{0,0}' \Psi_0(x_c) + 0^* \text{erf}(x_c) \]
\[ p_{0,0} = p_{0,0}' \Psi_0(x_D) + c_D^* \text{erf}(x_D) \]
\[ \eta_{j,m} = \eta_{0,0} + \Psi_{(2j+m)/(2z+1)}(x_D), \quad j, m \geq 0 \]
(18)
where the \( \Psi^* \) are the functions defined by Koutek [13].

Substituting eqns. (9) and (17) in eqns. (13)–(15) and taking into account the properties of the \( \Psi \) functions [14,15], we obtain after some manipulation,
\[ a_{0,0} = 0^* \]
\[ b_{0,0} = c_D^* \]
\[ a_{j,m} = a_{0,0}(m), \quad b_{j,m} = b_{0,0} \]
(19)
\[ c_{j,m} = -K \sum_{i=0}^{j} \frac{a_{i,m}}{(j-i)!} \frac{p_{i,m}(z)}{p_{j,m}(z)}, \quad (c_{j,m} = c_{0,0}) \]
(20)
\[ c_{j,m-1} = \sum_{i=0}^{j} \frac{1}{(j-i)!} \left( a_{i,m-1} \right) \left( X_1 = 1 \right) b_{i,m-1} \]
(21)
where
\[ \rho_{j,m}(z) = \frac{2\Gamma(1 + (2j + m)/(2z + 1))}{\Gamma((1/2 + (2j + m)/(2z + 1)) \gamma_1 K_i} \]
(22)
\[ X_1 = 1 + (1 + K) \gamma_1 K_i \]
(23)
\[ X_2 = (1 + K)(1 + \gamma_1 K_i) \]
(24)
In turn, combining eqns. (19)–(21), one obtains
\[ a_{0,0} = 0, \quad j > 0; \quad a_{j,0} = 0, \quad j \geq 0 \]
(25)
\[ a_{0,m} = \frac{(0^* - (1 + K)K^*_D)}{X_2} \sum_{i=0}^{m} \rho_{0,i}(z), \quad m \geq 1 \]
(26)
\[ a_{j,m} = \frac{K^*_D}{j!} \sum_{i=0}^{m} \frac{a_{i,m-1}}{p_{j,m-1}(z)} \left( \frac{X_1 + p_{i,m-1}(z)}{p_{j,m-1}(z)} \right) \frac{a_{i,m-1}}{a_{j,m-1}} \]
(27)
From eqns. (3), (4), (6) and (7) the current, \( i \) is given by
\[ i = nFq(t) \sqrt{2z+1} D_c \left( \frac{d^{1/2}}{d x_c} \right)_0 \]
(28)
Finally, inserting in this expression eqns. (9), (17), (18) and (23)–(27) we obtain, after some algebraic rearrangement, the following solution for the dc polarographic response for mechanism (1):
\[ i \frac{i_{q}}{q} = A_1 - (1 + K)K_i A_2 \left( F(z, w) + \frac{K}{X_2} S(X, w) \right) \]
(29)
where
\[ i_{q} = nFq(t) \sqrt{2z+1} D_c \]
(30)
\[ c_T = 0^* + c_D^* \]
(31)
\[ c_T = 0^* / c_T; \quad A_2 = c_D^* / c_T; \quad A_1 + A_2 = 1 \]
(32)
\[ F(z, w) = \sum_{m=0}^{\infty} \frac{(-1)^m m^{m+1}}{p_{0,0}(z) \cdots p_{0,m}(z)} \]
(33)
\[ S(X, w) = \sum_{j=1}^{\infty} B_j(w) X^j; \quad B_j(w) = \sum_{m=2}^{\infty} E_{j,m} w^m \]
\[ E_{j,m} = \frac{E_{j,m-1}}{p_{j,m-1}(z)} = \frac{1}{j!} \frac{(-1)^m}{p_{0,0}(z) \cdots p_{0,m-1}(z) \left( 1 - \frac{p_{0,m-1}(z)}{p_{j,m-1}(z)} \right)} \]
\[- \sum_{i=1}^{l-1} \frac{E_{r,m-1}}{(i-1)!} \left( \frac{X_i}{E_{r,m-1}} + \frac{K}{p_{r,m-1}(z)} \right) \frac{E_{r,m}}{\frac{1}{E_{r,m-1}}} \]

\[E_{r,0} = E_{r,1} = 0\]

Note that eqn. (34) is a recurrence relationship that allows us to calculate the \(E_{r,m}\) coefficient and hence \(B_i(w)\) from the \(E_{r,m}, E_{r,m+1}, \ldots, E_{r,m-1}\) and \(E_{r,m-1}, E_{r,m-2}, \ldots, E_{r,1}\) coefficients. In addition, from eqns. (33) and (34) it is readily shown (see Appendix) that \(B_i(w)\) is given by the following closed equation:

\[B_i(w) = \frac{p_{r,1}(z) p_{r,2}(z)}{w^r} \left\{ F(z, w) - \frac{1}{P_{r,0}} \right\} + \frac{p_{r,2}(z)}{P_{r,0}} - F(z, w) \]

(35)

On the other hand, for values of \(w \gg 1\), convergence of eqn. (33) is slow and under these conditions it is useful to employ an asymptotic solution of that equation. This solution is obtained by expanding in eqns. (9) \(s_i, \phi_i\) and \(c_i\) as powers of \(w^{-m}\) and proceeding as previously. Therefore, we find

\[\frac{i}{i_{d}} = \frac{A_1 - (1 + K)K_1 A_2}{X_2} \left\{ F(z, w) - \frac{K}{X_2} S_z(x, w) \right\} \]

(36)

where

\[F(z, w) = 1 + \sum_{j=1}^{\infty} (-1)^j \left( \prod_{i=1}^{j} P_{r,i-1}(z) \right) w^{-j} \]

\[s_z(x, w) = \sum_{j=1}^{\infty} C_j(w) x_j; \quad C_j(w) = \sum_{m=0}^{j} \epsilon_{j,m} w^{-m} \]

\[\epsilon_{j,m} = \frac{1}{j!} \left( \frac{P_{r,j-1}(z)}{P_{r,j-1}(z)} - 1 \right) \frac{1}{P_{r,0}} \prod_{i=0}^{m} p_{r,i-1}(z) + \epsilon_{j,m-1} p_{r,m-1}(z) \]

\[- \sum_{i=1}^{j-1} (i-1)! \left( \frac{1}{X_2} \left( \frac{X_i}{p_{r,m-1}(z)} + \frac{K}{\epsilon_{r,m} p_{r,m}(z)} \right) + \epsilon_{r,m} p_{r,m}(z) \right) \]

(39)

In short, eqns. (29) and (36) describe completely the problem for mechanism (1), and they allow us easily to obtain the corresponding equations both for a DME (by writing \(z = \frac{1}{2}\)) and for a stationary electrode (\(z = 0\)). (Note that as expected, \(i_d\) in eqn. (30) differs by the factor \(7/30\) for \(z = \frac{1}{2}\) and \(z = 0\) respectively.)

In addition, from these equations we may easily obtain the corresponding expressions for other particular cases. Thus, for example, if \(k_2 = K = 0\), eqn. (29) (or 36) becomes

\[\frac{i}{i_d} = \frac{A_1 - K_1 A_2}{1 + K_1} F(z, w) \]

(40)

This equation for \(z = \frac{1}{2}\) is identical with the expression derived earlier by Koutecký for the process \(C + n e^- \Rightarrow D\). When only species C is initially added to the solution, i.e., \(C_0 = 0, A_1 = 0, A_2 = 0\), eqn. (40) adopts the well-known form \(i/i_d = F(w)/(1 + K_1)\), where \(F(w) = (F'_{1/2} w)\) is the Koutecký function. In turn, introducing in eqn. (40) the \(p_{r,0}(0)\) values (see eqn. 22) and making \(\lambda = \frac{1}{2}(k_1 D/3 + k_r D/4) \quad (= w/2\text{, see eqn. 7 with } z = 0)\)

\[i_d = \frac{\sigma_{1/2} \lambda \exp(\lambda^2) \text{erfc}(\lambda)}{1 + K_1} \]

(35)

which is the corresponding equation for a stationary electrode under these conditions [4]. On the other hand, if we consider Nb, it follows that \(k_r \ll 1, w \gg 1\) and eqn. (36) gives

\[\frac{i}{i_d} = \frac{A_1 - (1 + K)K_1 A_2}{X_2} \left[ 1 + \frac{K}{X_2} \sum_{j=1}^{\infty} \epsilon_{j,0} X_{j} \right] \]

(41)

where

\[\epsilon_{j,0} = \frac{1}{j!} \left( \frac{p_{r,j}(z)}{p_{r,j}(z)} - 1 \right) \frac{1}{X_2} \sum_{k=1}^{j} \frac{p_{r,k}(z)}{p_{r,k}(z)} \]

(42)

For \(z = \frac{1}{2}\), eqn. (41) becomes identical with the equation previously derived by Galvez et al. [8] by adopting Nb.

Finally, the limiting current is also readily obtained by inserting in eqn. (41) the conditions \(K_1 = 0\) (cathodic limiting current) and \(K_1 \to \infty\) (anodic limiting current)

\[\frac{i}{i_d} = \frac{A_1}{1 + K_1} \left( 1 + \frac{K}{1 + K_1} \sum_{j=1}^{\infty} \epsilon_{j,0} X_{j} \right) \]

(43)

\[\frac{i}{i_d} = \frac{A_2}{1 + K_1} \left( 1 + \frac{K}{1 + K_1} \sum_{j=1}^{\infty} \epsilon_{j,0} X_{j} \right) \]

(44)

**EC mechanism**

For the process the electrode process is described by

\[D + n e^- \Rightarrow B \stackrel{k_1}{\rightarrow} C \]

(II)

and the dc polarographic response can be obtained by proceeding analogously to the CE mechanism. However, in this case the corresponding equations are obtained by replacing \(n, K\) and \(K_1\) by \(-n, 1/K\) and \(1/K_1\) respectively in the equations deduced
above for mechanism (I). Thus, we find
\[
\frac{i}{i_\alpha} = \frac{(1 + K)A_2 - KK_i A_1}{X_i} \left\{ F(z, w) + \frac{K_i}{X_i} T(X, w) \right\}
\] (45)
where
\[
T(X, w) = \sum_{j=1} J_j D_j(w)^\gamma; \quad D_j(w) = \sum_{m=2} F_{j,m} \omega^m
\] (46)
\[
F_{j,m} + \frac{F_{j,m-1}(z)}{P_{j,m-1}(z)} = \frac{1}{j!} \left\{ \frac{1}{\prod_{i=0}^{j-1} p_{i,m-1}(z)} \cdot \frac{1}{f_{j,m-1}(z)} \right\} (-1)^m \prod_{i=0}^{j-1} p_{i,m-1}(z) - p_{j,m-1} p_{j,m}(z)
\] (47)
\[
X_j = (1 + K)(\gamma_i + K_i)
\] (48)
\[
X_j = K + (1 + K)/K_i
\] (49)
In turn, for the asymptotic solution we have
\[
\frac{i}{i_\alpha} = \frac{(1 + K)A_2 - KK_i A_1}{X_3} \left\{ F(z, w) + \frac{K_i}{X_3} T_\alpha(X, w) \right\}
\] (50)
where
\[
T_\alpha(X, w) = \sum_{j=1} J_j G_j(w)^\gamma; \quad G_j(w) = \sum_{m=0} p_{j,m} \omega^m
\] (51)
\[
p_{j,m} = \frac{1}{j!} \left\{ \frac{P_{j,m}(z)}{P_{j,m}(z)} \right\} (-1)^m \prod_{i=0}^{j-1} p_{i,m-1}(z) - p_{j,m-1} p_{j,m}(z)
\] (52)
\[
j > 0, m \geq 0
\]
If \( k_2 = K = 0 \), eqns. (45) and (49) become
\[
\frac{i}{i_\alpha} = \frac{A_2}{\gamma_1 + K_1} \left\{ F(z, w) + \frac{K_j}{\gamma_1 + K_1} T^0(X, w) \right\}
\] (53)
where \( T^0(X, w) = T(X, w) \) if eqn. (45) is used and \( T^0(X, w) = T_\alpha(X, w) \) if we consider the asymptotic solution (eqn. 49) (\( A_1 \) and \( A_2 \) have the same meaning in both mechanisms).

On the other hand, if we consider Nb, eqn. (49) gives
\[
\frac{i}{i_\alpha} = \frac{(1 + K)A_2 - KK_i A_1}{X_3} \left\{ 1 + \frac{K_j}{X_3} \sum_{j=1} p_{j,0} \omega^j \right\}
\] (54)
These equations for \( z = \frac{1}{2} \) have also been derived previously [8], as in the CE mechanism.

In order to obtain the cathodic limiting current, we make \( K_i = 0 \) in eqn. (53), giving
\[
\frac{i_{cl}}{i_\alpha} = \frac{A_2}{1 + K}
\] (55)
In addition, if we make \( K_1 \rightarrow \infty \), we have the anodic limiting current as follows:
\[
\frac{i_{al}}{i_\alpha} = \frac{-KA_1}{1 + K} \left\{ 1 + \frac{1}{1 + K} \sum_{j=1} p_{j,0} \omega^j \right\}
\] (56)

RESULTS AND DISCUSSION

The discussion consists of two parts. In the first, we shall present some examples which show the general characteristics of the current–potential (I/E) curves with nNb for both mechanisms (because these characteristics have already been discussed, both in the context of the ssa [1-5, 16] and with the aid of numerical methods [12], we have not given special emphasis to this aspect of the problem). In the second, we shall discuss the strategy to follow in order to determine \( K, k_1 \), and \( k_2 \) as well as the charge-transfer rate parameters. For simplicity, calculations have only been carried out for a DME (\( z = \frac{1}{2} \)), although it is clear from the above theory that the results obtained for other values of \( z \) should be similar.

Current–potential curves

For convenience, the results of this section have been obtained for \( n = 1 \) and \( D_e = D_0 \) (\( \gamma_1 = 1 \)). In addition, the limit case for Nb (\( k_1 \rightarrow \infty \)) is also included for comparison.

CE mechanism

Figure 1 shows I/E curves computed from eqns. (29) and (36) when \( A_1 = 1 \) (i.e. \( c_0^2 = 0 \) and different values of \( K_1 \) (\( \chi = 1 \); \( K = 1 \); \( \alpha = 0.5 \)). In turn, Fig. 2 shows the corresponding I/E curves when species B, C and D are initially added to the solution. Note how in this case the anodic limiting current is independent of the kinetic parameters of the chemical reaction due to the fact that under these conditions \( (E \rightarrow +\infty) \), mechanism (I) behaves as an EC mechanism.

Figure 3 illustrates the effect of the reversibility of the chemical reaction on the I/E curves for \( \chi = 2.5 \). These waves show—indepedently of whether they are
Fig. 1. CE mechanism: $I/E$ curves (eqns. 29 and 36) with $A_1 = 1$, $n = 1$, $T = 298$ K, $D_h = D_c = D_{ij} = 10^{-3}$ cm$^2$ s$^{-1}$, $t = 3$ s, $K = 1$, $x = 1$, $a = 0.5$, $k_i$ (cm s$^{-1}$): (A) $\infty$; (B) $10^{-2}$; (C) $10^{-3}$; (D) $10^{-4}$; (E) $10^{-5}$.

Fig. 2. CE mechanism: dependence of the $I/E$ curves on $A_2$: $k_i$ (cm s$^{-1}$): (——) $10^{-3}$; (· · · ·) $\infty$; $A_2$: (A) 0.1; (B) 0.5; (C) 0.9. Other conditions as in Fig. 1.

Fig. 3. CE mechanism: dependence of the $I/E$ curves on $K$, $x = 2.5$; $k_i$ (cm s$^{-1}$): (——) $10^{-3}$; (· · · ·) $\infty$; $K$: (A) 0.1; (B) 0.5; (C) 1; (D) 2; (E) 5; (F) 10. Other conditions as in Fig. 1.

Fig. 4. CE mechanism: $I/E$ curves computed with the rigorous solution (eqns. 29 and 36) (——) and with the ssa (· · · ·). (I) $k_i = 10^{-3}$ cm s$^{-1}$, $x = 2.5$; (II) $k_i = 10^{-4}$ cm s$^{-1}$, $x = 0.5$. Other conditions as in Fig 1.
reversible or irreversible—a shift towards negative potentials and, at the same time, a diminution of the cathodic limiting current as $K$ increases.

Regarding the validity of the ssa, in Fig. 4 we have plotted $I/E$ curves computed from rigorous equations and those obtained with the ssa [16]. As expected, larger deviations are found as $\chi$ decreases (see ref. 8 for further discussion).

**EC mechanism**

Figure 5 illustrates the effects of the reversibility of the charge-transfer reaction on the $I/E$ curves when the chemical reaction is irreversible ($K = 0$). Note that the cathodic limiting current does not depend on the kinetic parameters, in accordance with eqn. (55).

In Fig. 6 we have obtained $I/E$ curves computed both with the rigorous theory and with the ssa [16]. As previously, deviations increase as $\chi$ becomes smaller. In any case, due to the fact that both approaches predict that $i_{\text{r,c}}/i_{\text{u}} = 1$, it follows in this case that the error introduced by the use of the ssa is smaller than for a CE mechanism.

**Quantitative kinetic data analysis**

In this section we shall first make the exposition for the CE mechanism. Adaptation for the EC mechanism is shown later.

Quantitative evaluation of data obtained from mechanism (I) varies in complexity, depending on the kinetic situation. Thus, it is clear that the existence of two slow processes (charge-transfer and chemical reaction kinetics) in addition to diffusion makes the data analysis problem more complex. In any case, taking into account the theory developed above one finds that the following strategy can be adopted:

1. Determination of the kinetic parameters of the chemical reaction. This can be more easily carried out through measurements of the limiting current values because they are independent of the charge-transfer kinetics. Thus, we may obtain working
curves of $i_{te}/i_d$ as a function of $K$, $k_1 + k_2$ and $t$ only (see eqn. 43). These working
curves allow us to determine $k_1$ and $k_2$ if the $K$-value is known (see ref. 8 for details).
In addition, these curves also allow the $K$-value to be obtained under certain
conditions. However, this aspect of the problem was not discussed in ref. 8 and for
this reason we present here the procedure to follow. Thus, from eqn. (43) one finds
that if the $x$-values are $\leq 0.3$ the relationship $i_{te}/i_d$ is given by

$$ I_t = \frac{1}{1 + K} \left( 1 + \frac{k_1 x}{2} \right) $$

or

$$ \frac{1 - I_t}{I_t} = K - \frac{(1 + K) k_1 x}{2} $$

(57) (58)

From eqn. (58) it follows that for these $x$-values a plot of $(1 - I_t)/I_t$ vs. $t$ must be
linear with slope $-(1 + K) k_1 x/2$ and intercept $K$ [the corresponding plot from eqn.
(57) gives $k_1/(2(1 + K))$ and $1/(1 + K)$ respectively]. Thus, in Fig. 7 we show the
dependence of $(1 - I_t)/I_t$ vs. $x$ computed from eqn. (58) and also that obtained
from eqn. (43). Deviations between both equations increase as $x$ becomes greater,
although as mentioned above, a good agreement is found if $x \leq 0.3$. In this practice,
$I_t$-values as a function of $t$ may be obtained by shortening the drop time. In
principle, this could be achieved by increasing mercury column height, but a much
more convenient method is to use dc polarography with short controlled drop times
[17]. In this way, $t$-values of $\sim 0.1$ s may be achieved, so that eqns. (57) and (58)
remain valid when $k_1 + k_2$ is $\sim 3$ s$^{-1}$ or less. This then allows $K$, $k_1$ and $k_2$ to be
determined.

On the other hand, it is interesting to show that in the cases where the chemical
reaction is pseudo-first order we may also follow an alternative strategy, based on
obtaining $I$-values when species B, C and D are initially added to the solution. Thus,
if $I(0)$ and $I(1)$ are the $I$-values for $A_2 = 0$ and $A_2 = 1$ respectively, from eqn. (29)
one obtains

$$ I(0) = \frac{1}{(1 + K) K_1} $$

(59)

or

$$ E = E^0 - \frac{RT}{nF} \ln \left( \frac{I(0)}{I(1)} \right) - \frac{RT}{nF} \ln(1 + K) $$

(60)

Now, if mechanism (I) is written

$$ B + Z \underset{k_1}{\stackrel{k_2}{\rightleftharpoons}} C + n e^{-z \varphi} D $$

(61)

we have $k_1 = k_2 e^{-z \varphi}$ and the value of $K$ is given by

$$ K = K_1 c_2; \quad K_1 = k_2/k_1' $$

(62)

where $c_z$ represents the bulk concentration of an electroinactive species $Z$ which can
be made much larger than that of substance B. Combining eqns. (60) and (61) we obtain

$$ K_1 = c_z e^{-z \varphi}/(f - 1)/(c_1 - c_2 f) $$

(63)

where $I(0)$ and $I(1)$ are $I$-values at potential $E$, and $c_z = c_1$

$$ f = \left[ I(0)/I(1) - I(0)/I(1) \right] \exp(nF(E_1 - E_2)/RT) $$

(64)

(2) Determination of the $I/E$ curve under Nb. This objective, i.e. the dependence
of $I_{te}$ on $E$ may be obtained once the kinetic parameters of the chemical reaction
have been determined and provided that the $E^*$-value is also known (see eqn. 60) (if
this value is unknown, a possible procedure to follow is through measurements of
$I(0)$ and $I(1)$ values and taking into account eqn. 60).

(3) Evaluation of the charge-transfer rate parameters. Comparison of eqns. (36)
and (41) suggests the convenience of using the approximate equation

$$ I \approx I_{te} e^{-F(x)} $$

Fig. 7. CE mechanism: dependence of $(1 - I_t)/I_t$ on $x$: (———) eqn. (43); (-----) eqn. (58). (I) $K = 5$;
(II) $K = 2$. Other conditions as in Fig. 1.
for the kinetic data analysis. In Fig. 8 we have plotted I-values vs. E obtained from eqn. (64) and those computed with eqn. (29) or (36). Note that deviations are maximum for E-values ~ E_{1/2}. However, good agreement exists for other values of E so that the error introduced by eqn. (64) decreases as w becomes larger, i.e. both at the foot and at the top of the wave. Under these conditions one may obtain F(w)-values vs. E from eqn. (64), and therefore evaluate the charge-transfer rate parameters by using well-established procedures [18–20]. Finally, a further refinement is accomplished by using these parameters as trial values in an iterative procedure in order to construct the theoretical working curve which matches best the shape of the corresponding experimental plot.

In short, step (1) provides kinetic parameters of the chemical reaction, while step (3) gives the charge-transfer rate parameters provided that the I_{ref}-values in step (2) are obtained.

**EC mechanism**

In this case, if we consider that only species D is initially added to the solution it follows that the I_{ref}-value is independent of the kinetic parameters of the chemical reaction and hence, step (1) described above is unworkable. However, it is readily shown that the kinetic analysis made above for the CE mechanism also remains valid, if species B and C are initially present in the solution.

**APPENDIX**

From eqn. (34) one finds that the E_{1,m} value is given by

\[
E_{1,m} = (-1)^m \frac{p_{0,m}(z) p_{0,m+1}(z) - p_{0,1}(z) p_{0,2}(z)}{\prod_{i=0}^{m+1} p_{0,i}(z)} \tag{A1}
\]

In turn, from eqn. (33) we have

\[
B_i(w) = \sum_{m=2}^{\infty} E_{1,m} w^m \tag{A2}
\]

Introducing in this expression eqn. (A1) and taking into account eqn. (32), one easily obtains eqn. (35) after some manipulation.

**REFERENCES**

18. Ref. 17, p. 100.