Chronopotentiometry with non-linear perturbation functions at the DME with a preceding blank period

Electrode curvature effects and experimental verification

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ABSTRACT

The effect of electrode curvature on $E-t$ curves obtained in chronopotentiometry with non-linear perturbation of the form $I(t) = I_{0} e^{w}$ ($w \approx -1/2$) after a blank period, $t_{b}$, at the DME, is presented. The cases where the reduction product dissolves both in the electrolyte solution and in the electrode are considered. Concentration profiles have been obtained, and reversibility criteria and methods for determining kinetic parameters of the charge transfer reaction are proposed. The theory has been experimentally verified with Fe(III)/Fe(II), Ti(III)/Ti(Hg), Cr(III)/Cr(II), and Zn(II)/Zn(Hg) using a linear current scan and a current step. The kinetic parameters of the two last systems have been determined.

INTRODUCTION

Chronopotentiometry with programmed current has been developed largely for both stationary [1,2] and unstationary electrodes [3]. In a previous paper [4] we have developed the theory corresponding to chronopotentiometry with a programmed current, of the form $I(t) = I_{0} t^{w}$, at a DME with a preceding blank period, by using the expanding plane electrode model and restricting the discussion to $w \approx 0$. In this paper, the treatment is extended to $w \approx -1/2$, taking into account also the influence exerted by the sphericity of the electrode. The use of $w < 0$ is not too interesting from the experimental point of view. (This requires $I(t) \to \infty$ when $t \to 0$), but it is very interesting from the theoretical point of view, owing to the special features of $E-t$ curves in the latter case. We have studied both the situation where the two species are soluble in the electrolyte solution, as well as where the reduced
one is soluble in the electrode (amalgam formation), and we have obtained the corresponding concentration profiles in both cases.

The theoretical equations deduced here were applied to the experimental systems Fe(C₅H₅N)³⁺/Fe(C₅H₅N)²⁺, Ti⁺⁺/Ti(Hg), Cr³⁺/Cr²⁺ and Zn²⁺/Zn(Hg), which practically include all possibilities in a simple charge transfer reaction, discussing, among other effects, the influence exerted by \( w \) in reversibility.

**THEORY**

If we consider the charge transfer reaction

\[
A + n e^{-} \xrightarrow{k_1} B
\]

the expanding sphere boundary value problem is given by

\[
\hat{D}_A \xi_A = \hat{D}_B \xi_B
\]

\[
t = 0, \ r > r_0
\]

\[
t > 0, \ r \to \infty
\]

\[
t > 0, \ r = r_0
\]

\[
\hat{D}_A \left( \frac{\partial \xi_A}{\partial r} \right)_{r=r_0} = -\hat{D}_B \left( \frac{\partial \xi_B}{\partial r} \right)_{r=r_0} = \frac{I(t)}{nFA(t_0)}\]

\[
I(t)/nFA(t_0) = k_I c_A(0, t) - k_I c_B(0, t)
\]

where \( \hat{D} \) is the operator

\[
\hat{D} = \frac{\partial}{\partial t} - \hat{D} \left( \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right)^{\frac{a}{3}} \frac{\partial}{\partial r}
\]

and

\[
k_I = k_s \exp\left\{ \frac{-\alpha nFRT}{E_0} \right\}
\]

\[
k_B = k_s \exp\left\{ \frac{(1-\alpha)nFRT}{E_0} \right\}
\]

\[
t = t_0 + t
\]

\[
I(t) = I_0 t^\gamma, \quad w = -1/2
\]

If we expand \( c_A \) and \( c_B \) as

\[
c_A(s_A, \xi_A, x, \beta) = c_A^* + \sum_{i,j,k} g_{i,j,k}(s_A) \xi_A^i x^j \beta^k
\]

\[
c_B(s_B, \xi_B, x, \beta) = c_B^* + \sum_{i,j,k} \Phi_{i,j,k}(s_B) \xi_B^i x^j \beta^k
\]

we may find the solution of eqns. (1)–(3) (see ref. 4 and Appendix) so that the general expressions for \( c_A \) and \( c_B \) are

\[
c_A(s_A, \xi_A, x, \beta) = c_A^* + N(m, t, t_0) \left( \sum_{n=0}^{2} \sum_{i,j,k} \sigma_{i,j,k}(s_A) \xi_A^i \beta^k \right)
\]

\[
c_B(s_B, \xi_B, x, \beta) = c_B^* + N(m, t, t_0) \left( \sum_{n=0}^{2} \sum_{i,j,k} \sigma_{i,j,k}(s_B) \xi_B^i \beta^k \right)
\]

where

\[
N(m, t, t_0) = N_t \beta^m t^\gamma
\]

\[
N_t = 2I_0/nFA(t_0)
\]

\[
m = w - 1/6
\]

\[
\gamma = (D_A/D_B)^{1/2}
\]

and superscript “*” relates to the Koutecký function used (see Appendix).

If \( s = 0 \) we obtain the surface concentrations of \( A \) and \( B \) as functions of \( t \)

\[
c_A(s_A, \xi_A, x, \beta) = c_A^* - c_A^* N(m, t, t_0) \left[ F(m, \beta) - \xi_A F_1(m, \beta) + \xi_A^2 F_2(m, \beta) \right]
\]

\[
c_B(s_B, \xi_B, x, \beta) = c_B^* + \gamma c_A^* N(m, t, t_0) \left[ F(m, \beta) - \xi_B F_1(m, \beta) + \xi_B^2 F_2(m, \beta) \right]
\]

where

\[
F(m, \beta) = \frac{1}{P_{m,A}} + A(m) \beta^2 + B(m) \beta^4 + C(m) \beta^6 + \ldots
\]

\[
A(m) = \frac{1}{(6m+10)} \frac{1}{P_{m,A}}
\]

\[
B(m) = \frac{7}{2(6m+10)(6m+16)} \frac{1}{P_{m,A}}
\]

\[
C(m) = \frac{20}{(6m+10)(6m+16)(6m+22)} \frac{1}{P_{m,A}}
\]

\[
F_1(m, \beta) = A_1(m) + B_1(m) \beta^2 + C_1(m) \beta^4 + \ldots
\]
\[ A_1(m) = \frac{3}{2(6m + 7)} \]
\[ B_1(m) = \frac{9}{2(6m + 7)(6m + 13)} \]
\[ C_1(m) = \frac{81}{4(6m + 7)(6m + 13)(6m + 19)} \]
\[ F_1(m, \beta) = A_2(m) + B_2(m)\beta^3 + \ldots \]
\[ A_2(m) = \frac{1}{2(6m + 10)} \rho_{m,A} \]
\[ B_2(m) = \frac{1}{9(6m + 10)(6m + 16)} \rho_{m,A} \]

Equations (12)–(25) are valid if \( w \approx -1/2 \) (\( m \approx -2/3 \)).

**Transition Time**

The transition time, \( \tau \), is obtained from eqn. (18) by writing \( c_A(\tau_0, \tau) = 0 \). Thus we have

\[ \frac{1}{N} - \tau^w \beta^2 \left\{ F(m, \beta_1) - \xi_{0,A} \beta \tau^{w} F_1(m, \beta_1) + \xi_{0,A} \beta \tau^{w} F_2(m, \beta_1) \right\} \]

where

\[ \xi_{0,A} = \frac{2D_1^{1/2}}{a} \]

and \( \beta_i \) is the value of \( \beta \) for \( t = \tau_i \).

Equation (26) can be rewritten in normal polarographic units (\( \tau \); \( m_{\text{Hg}} \text{ mg s}^{-1} \); \( D_1 \text{ cm}^2 \text{ s}^{-1} \); \( c_A^* \text{ mM} \); \( \rho_{m,A} \text{ mA} \text{s}^{-1} \)) at 298 K as

\[ \frac{410.125m_{\text{Hg}}^{2/3}D_1^{1/2}c_A^*}{I_0} = \tau^{w} + \frac{76.9554D_1^{1/2}}{m_{\text{Hg}}^{2/3}} \beta \tau^{w} F_1(m, \beta_1) + \frac{592.13D_1^{1/2}}{m_{\text{Hg}}^{2/3}} \beta \tau^{w} F_2(m, \beta_1) \]

If \( t_1 \to 0 \) (which implies \( w \approx 1/6 \)), eqn. (26) is equivalent to eqn. (17) in ref. 5. If \( t_1 \gg t \), eqn. (26) gives

\[ \frac{nFA_1D_1^{1/2}c_A^*}{2I_0} = \tau^{w} + 2/3 \left\{ \frac{1}{\rho_{m,A}} - \frac{3D_1^{1/2}t^{1/2}}{r_0(6m + 7)} \right\} + \frac{6D_1 t^{1/2}}{r_0(6m + 10)} \rho_{m,A} \]

where \( A \) is the electrode area when current is applied (= \( A_1 t^{1/2} \)). Equation (29) is identical to that obtained for a spherical stationary electrode [6], and is equivalent to that of Delahay and Mamantov [7] and Koutecký and Cizek [8] when \( w = 0 \).

**Potential–Time Functions (p(t))**

The dependence of \( E(t) \) on \( t \) may be obtained in a dimensionless form by making the substitutions

\[ \theta(t) = \theta_0 t \]
\[ \beta = c_A^* / c_A \]

and introducing eqns. (30)–(33) in eqn. (34)

\[ \begin{align*}
\theta(t) &= -N(m, t, t_1) \left\{ F(m, \beta) - \xi_{0,A} F_1(m, \beta) + \xi_{0,A} \beta \tau^{w} F_2(m, \beta) \right\} \\
&\quad -10^{w+1} \left\{ \mu + nF(m, t, t_1) \right\} \left[ F(m, \beta) - \xi_{0,A} F_1(m, \beta) + \xi_{0,A} \beta \tau^{w} F_2(m, \beta) \right] \\
\end{align*} \]

For \( k_s \to \infty \) (Nernstian behaviour), eqn. (34) becomes

\[ \eta(t) = \frac{1}{\alpha} \log \frac{N(m, t, t_1)}{N(m, t_1)} \left[ F(m, \beta) - \xi_{0,A} F_1(m, \beta) + \xi_{0,A} \beta \tau^{w} F_2(m, \beta) \right] \]

which can be rewritten (if \( \mu = 0 \))

\[ E(t) = E_{1/2} + \frac{RT}{nF} \log \frac{1 - N(m, t, t_1)}{N(m, t_1)} \left[ F(m, \beta) - \xi_{0,A} F_1(m, \beta) + \xi_{0,A} \beta \tau^{w} F_2(m, \beta) \right] \]

If \( k_s \to 0 \) (totally irreversible process), eqn. (34) simplifies to

\[ \eta(t) = \frac{1}{\alpha} \log \frac{1 - N(m, t, t_1)}{N(m, t_1)} \left[ F(m, \beta) - \xi_{0,A} F_1(m, \beta) + \xi_{0,A} \beta \tau^{w} F_2(m, \beta) \right] \]

or

\[ E(t) = E_0 + \frac{RT}{nF} \log \frac{1 - N(m, t, t_1)}{N(m, t_1)} \left[ F(m, \beta) - \xi_{0,A} F_1(m, \beta) + \xi_{0,A} \beta \tau^{w} F_2(m, \beta) \right] \]

where

\[ g(m, \beta, \xi_{0,A}) = \frac{1}{\beta} \tau^{w} \left[ F(m, \beta) - \xi_{0,A} F_1(m, \beta) + \xi_{0,A} \beta \tau^{w} F_2(m, \beta) \right] \]

**Amalgam Formation**

In this case we must rewrite the boundary value problem as follows

\[ t = 0, r > r_0: \quad c_A = c_A^*, \quad c_B = 0 \]
\[ t > 0, r \to \infty: \quad c_A = c_A^* \]
\[ t > 0, r = r_0: \quad \frac{\partial c_A}{\partial r} \bigg|_{r=r_0} = \frac{D_1}{r_0} \frac{\partial c_B}{\partial r} \bigg|_{r=r_0} \]
The procedure of derivation followed, using these new conditions, differs slightly from that adopted in the preceding section. In this case, no difference is observed in \( c_A(s_A, \xi_A, \chi, \beta) \) with the preceding one (eqn. 12). However, we obtain for \( c_B \)

\[
c_B(s_B, \xi_B, \chi, \beta) = c_B^0 + \gamma N(m, \beta, t_1) \left( \sum_{n=0}^{\infty} \sum_{l=0}^{\infty} (-1)^{l+1} \sigma_{l,3n+2}^r s_B \xi_B^l \beta^{2n} \right) \tag{43}
\]

where superscript "+" relates to the Koutecky functions used (see Appendix).

So, pt's can be rewritten in the following generalized form

\[
\theta(t) - \tau_0 = N(m, \beta, t_1) \left( F(m, \beta) - \xi_A F_1(m, \beta) + \xi_B F_2(m, \beta) \right)
\]

\[
-10^{(1/10)} \left( \mu + \gamma N(m, \beta, t_1) \left[ F(m, \beta) - \xi_A F_1(m, \beta) + \xi_B F_2(m, \beta) \right] \right) \tag{44}
\]

where the upper sign relates to a solution soluble product, and the lower one to the amalgamation reaction (this rule will be followed in the next sections).

RESULTS AND DISCUSSION

Figures 1–3 show the concentration profiles of species A and B, when both are soluble in the electrolyte solution (Figs. 1 and 2) and when B is amalgamated into the electrode (Fig. 3). From these graphs it is evident that the concentration gradient of A, \( \partial c_A / \partial r \), in the vicinity of the electrode increases with electrolysis time if \( w > 1/6 \). If \( w < 1/6 \), the behaviour is \( N_e \)-dependent. So, when \( N_e < (N_e)_{\text{min}} \) (see below), \( \partial c_A / \partial r \) increases first and decreases later. As a consequence, no depletion of A is observed on the electrode surface and no transition time occurs (Fig. 2).

When amalgamation takes place, \( c_B / c_A^0 \) increases above unity. This fact (which is not observed if both species are soluble in the electrolyte solution) is due to the restriction of diffusion of B inside the electrode. Several authors have questioned the unconditional validity of the boundary conditions given in eqn. (41) with spherical stationary electrodes [9,10]. With a spherical expanding electrode, we have never observed a variation of \( c_B \) near the centre of the electrode (Fig. 3), even in the most unfavourable situations (high sphericity, extreme electrolysis times, \( D_A > 5 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1} \text{ etc.} \)), which indicates that this boundary condition is always valid for this electrode.

In Table 1 we have calculated transition times by using the expanding plane model, \( \tau_r \), with first-order, \( \tau_1 \), and also with second-order, \( \tau_2 \), spherical correction, for several values of \( w \). As can be observed, the influence exerted by the sphericity of the electrode on the transition time is always important, and increases when \( w \) diminishes. Consequently, the applicability of the expanding plane electrode model is limited to electrodes with slight sphericity and with \( w \) far from its minimum value. Likewise, second-order spherical correction is only significant when \( w < 1/6 \).

On the other hand, if \( N_e > 3 \times 10^{-2} \text{ s}^{-1} \), \( \tau_1 \) increases with \( w \). However, if \( N_e < 3 \times 10^{-2} \text{ s}^{-1} \), the effect is the opposite (in both cases, we have supposed that \( t_1 = 2 \text{ s}, \xi_{0,A} = 0.2 \text{ s}^{-1/6} \) and \( w < 2 \)). This fact is due to the different behaviour of the perturbation, \( H(t) \), with \( w \), depending on whether \( t \) was greater or smaller than 1.

Equation (18) can be rewritten as

\[
\frac{c_A(s_A, \xi_A, \beta)}{c_A^0} = \frac{1}{N_e} H(m, \beta, \xi_{0,A}, t) \tag{45}
\]
where

$$H(m, \beta, t, \xi_{0,A}) = \beta^2 \xi^m \left[F(m, \beta) - \xi_{0,A} \beta^{1/3} F_1(m, \beta) + \xi_{0,A}^2 \beta^{2/3} F_2(m, \beta)\right]$$  \hspace{1cm}(46)$$

If \( w > 1/3 \), \( H \) has no upper bound on \( t \). Under these conditions we can always find a \( t \) value (equal to \( \tau \)) in such a way that \( H = 1/N_t \). However, if \(-1/2 < w \leq 1/6\), there is an upper limit \((1/(N_t)_{\text{max}})\) in \( H \) (Fig. 4). If \( N_t < (N_t)_{\text{max}} \) there is no transition time in the corresponding \( E \)-\( t \) curve; conversely, if \( N_t > (N_t)_{\text{max}} \), the transition time is the corresponding abscissa value in the rising part of the curve.

On the other hand, if only first-order spherical correction is taken into account, eqn. (28) can be rewritten as

$$D_A^{1/2} = \frac{\tau^{m_0} \beta_l^2 F(m, \beta_0)}{410.125nm^{3/2}c_A + 76.9554 \frac{\tau_0}{m_{1/3}^1} \beta_l^{m+1/6} F_1(m, \beta_0)}$$  \hspace{1cm}(47)$$

which offers an explicit expression for \( D_A \). Owing to the dependence of \( D_A \) on \( \tau \) (Fig. 3), it is possible to find the experimental conditions in which \( D_A \) can be determined, even if there is an important uncertainty in \( \tau \).

In the first stage of the current application, the \( E \)-\( t \) curve behaviour is strongly dependent on \( m_i \). If we suppose that only species \( A \) is present in solution, the following behaviour is observed: (a) Reversible process: If \( w > -1/2 \), then \( \Delta E_{t \to 0} \to \infty \) (Fig. 6, eqn. 36). (b) Totally irreversible process: if \( 0 > w > -1/2 \) then \( \Delta E_{t \to 0} \to -\infty \). If \( w = 0 \), then \( \Delta E_{t \to 0} = (RT/\alpha n F) \ln(n_i FA_0 c_A^{m_i/2}/I_0) \) [4]. If \( w > 0 \), then \( \Delta E_{t \to 0} \to \infty \) (Fig. 7, eqn. 38). (c) Quasi-reversible process: an intermediate behaviour is observed. This fact permits a qualitative differentiation between totally irreversible and reversible processes.

If \( w = -1/2 \), the \( E \)-\( t \) curves never show transition times. However, in this case, there is a maximum value of \( N_t \) (see eqn. (18), \( (N_t)_{\text{max}} = 2t^{1/3}/\tau^{1/2} \)) for which...
Fig. 9. Electrode curvature effects on $E-t$ curves (eqn. 36). $w = 0, N = 3.5 \, \text{s}^{1/4}$. Other conditions as in Fig. 8.

Fig. 10. Potential–time curves for a reversible process (eqn. 44). (a) Both species are soluble in the electrolyte solution; (b) B amalgams into the electrode. $w = 1, N = 2.5 \, \text{s}^{1/4}, t_i = 2 \, \text{s}, \xi_{\text{a,b}} = 0.4 \, \text{s}^{1/2}$. Other conditions as in Fig. 6.

Figures 8 and 9 show the effects exerted by electrode curvature on $E-t$ curves. These effects are maximal in transition time and more evident for the lower $w$ values. On the other hand, Fig. 10 shows the effect of amalgam formation on $E-t$ curves.

If $w > 1/6$, the behaviour of a charge transfer reaction in relation to reversibility is the same as described in refs. 4 and 5. However, a system behaves more irreversibly if $w$ decreases below this value. So, plotting $E$ vs. In $g(m, \beta, \xi_b)$ for a charge transfer reaction with $10^{-3} < \kappa < 10^{-2}$ (result not shown), the plots approach linearity as $w$ decreases; we can observe a quasi-reversible behaviour if $w > 1$ and an irreversible one if $w \leq -1/3$.

**EXPERIMENTAL**

**Material and procedures**

$E-t$ curves were obtained with an Amel 551 potentiostat–galvanostat, modulated by an Amel 567 function generator (linear scan) or an Amel 563 Electrometer and a Nicolet Explorer III digital oscilloscope. Hard copies of the $E-t$ curves were obtained with a Hewlett-Packard–Amel 862/D recorder.

Two DMEs were used, with mercury flow rates of 0.49 and 1.74 mg s$^{-1}$ when immersed in an aqueous 0.2 $M$ KNO$_3$ solution at $-1.0 \, \text{V}$ and at $h = 50$ and 35 cm, respectively.

All potentials are referred to the SCE. The temperature was $298 \pm 0.1 \, \text{K}$. Chemicals were of Merck reagent grade and they were dissolved in twice-distilled water. Mercury was first purified electrolytically and then distilled three times. We used a $5 \times 10^{-2} \, M$ stock solution of Fe(NO$_3$)$_3$, Ti(NO$_3$)$_3$, Cr(NO$_3$)$_3$ or Zn(NO$_3$)$_2$, acidified if necessary, to which K$_2$C$_2$O$_4$ (pH = 4.5), KNO$_3$, NaClO$_4$ or NaNO$_3$ were added.

$E-t$ curves were recorded using an expanding scale (approx. 300 mm in the paper chart) in such a manner that 1 mm was equivalent to 0.01–0.001 s. The transition time was assumed to be that at which a sudden jump in the curve was observed. When this sudden jump was ill-defined, the transition time was assumed to be that corresponding to the inflection point in the $E-t$ curve. In all cases the transition times measured in several experiments under the same conditions were reproducible to better than 0.01 s. In order to avoid distortion in the curves by non-faradaic processes, relatively concentrated solutions ($> 10^{-3} \, M$) were used. Taking into account that distortions not originating from faradaic processes or from the presence of trace impurities are more evident at the beginning and at the end of the $E-t$ curves, only the central part (approx. 80%) of these curves was considered in the kinetic measurements.

The approximate value of $E_{t=0}$ was obtained by extrapolating the $E-t$ curves, to $t > 0$, taking into account the morphology of $E-t$ curves for an irreversible process.

The $E^0$ value of Cr$^{3+}$/Cr$^{2+}$ was assumed to be $-650 \, \text{mV}$ and for Zn$^{2+}$/Zn(Hg) it was determined polarographically by means of Koryta’s method.

**EXPERIMENTAL RESULTS**

We obtained $E-t$ curves for four experimental systems: Fe(C$_2$O$_4$)$_3^{3-}$/Fe(C$_2$O$_4$)$_3^{2-}$, Ti$^3+$/Ti(Hg), Cr$^{3+}$/Cr$^{2+}$ and Zn$^{2+}$/Zn(Hg), using both a current step (Fig. 11) and a linear scan of current (Fig. 12). In all cases the $E-t$ curves were well defined and largely reproducible.

In Table 1 we have compared the transition times computed by eqn. (28), using for $D_\text{a}$ the values obtained from polarographic measurements under the same
conditions, with those obtained experimentally for 2.0 mM Ti⁺ in 0.2 M KNO₃. A very good agreement between them is observed. For the other systems, the results (not shown) are comparable.

Equation (36) can be rewritten as

$$ E = E'_{1/2} + \left( \frac{RT}{nF} \right) \ln g_s(m, \beta, \xi) $$

(48)

**TABLE 2**

Comparison of the τ values computed from eqn. (28), τ_{exp}, with those obtained from experimental E–t curves, τ_{exp}, for the reduction of Ti⁺ in 0.2 M KNO₃, D_{Ti⁺} = 1.72 × 10⁻¹⁰ cm² s⁻¹, c_{Ti⁺} = 2.0 mM.

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<td>4.20</td>
</tr>
<tr>
<td>0</td>
<td>0.49</td>
<td>13.5</td>
<td>3.0</td>
<td>0.93</td>
<td>0.94</td>
</tr>
<tr>
<td>0</td>
<td>0.49</td>
<td>15.0</td>
<td>3.0</td>
<td>0.46</td>
<td>0.46</td>
</tr>
<tr>
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<td>0.49</td>
<td>18.0</td>
<td>3.0</td>
<td>0.35</td>
<td>0.36</td>
</tr>
<tr>
<td>0</td>
<td>0.49</td>
<td>21.0</td>
<td>3.0</td>
<td>0.23</td>
<td>0.23</td>
</tr>
</tbody>
</table>

**TABLE 3**

Comparison between the values of α and kᵢ obtained in this work and literature values at 298 K for the system Cr³⁺/Cr²⁺.

<table>
<thead>
<tr>
<th>Medium</th>
<th>Reference</th>
<th>α</th>
<th>log(kᵢ/cm s⁻¹)</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5 M NaClO₄</td>
<td>*</td>
<td>0.59</td>
<td>-5.01</td>
<td>*</td>
</tr>
<tr>
<td>0.5 M NaClO₄</td>
<td>12</td>
<td>0.62</td>
<td>-5.05</td>
<td>CV</td>
</tr>
<tr>
<td>0.1 M HClO₄ + 0.9 M NaClO₄</td>
<td>13</td>
<td>0.45</td>
<td>-5.00</td>
<td>DCP</td>
</tr>
<tr>
<td>1.0 M NaClO₄</td>
<td>14</td>
<td>0.55</td>
<td>-5.30</td>
<td>CV</td>
</tr>
<tr>
<td>0.5 M NaClO₄</td>
<td>15</td>
<td>0.63</td>
<td>-5.10</td>
<td>NPP</td>
</tr>
</tbody>
</table>

* This work.
we obtained $\alpha = 0.6 \pm 0.05$ and log $k_2 = -5.2 \pm 0.2$. However, these should be regarded as estimations, because $\Delta E_{1/2}$ is obtained by extrapolation from each $E-t$ curve (see Experimental). In Fig. 13 we have plotted $\Delta E$ vs. $\ln g(m, \beta, \xi_A)$ for Cr$^{3+}$/Cr$^{2+}$, using a linear current scan for several values of $I_o$. In all cases a good linearity ($R > 0.995$) is obtained. From these plots we obtained $\alpha = 0.59 \pm 0.01$ and log $k_2 = -5.01 \pm 0.02$, in good accordance with the literature values (Table 3).

The system Zn$^{2+}$/Zn(Hg) in 0.5 M NaNO$_3$ shows a quasi-reversible character if $w = 1$ and an irreversible one if $w = 0$ (Fig. 14). From the data in Fig. 15, which also show good linearity ($R > 0.9992$), we obtained $\alpha = 0.28 \pm 0.01$ and log $k_2 = -2.29 \pm 0.02$, in agreement with reports in the literature (Table 4).

APPENDIX

The differential eqns. (1) with the variables (11) and taking into account eqn. (10), become the following recurrent differential equations (which depend only on $s_j$):

$$\sigma_{i,j,k}(s_{j,k}) + 2 s_{j,k} \phi_{i,j,k}(s_{j,k}) - (i + 2 mj + \frac{3}{2} k) \sigma_{i,j,k}(s_{j,k})$$

$$= - \left\{ \sum_{f+i=1} e_f \sigma_{i,f,j,k}(s_{j,k}) + \sum_{r+p=i} d_r \phi_{r,j,k-1}(s_{j,k}) + \frac{2}{3} (i + k - 3) \sigma_{i,j,k-1}(s_{j,k}) \right\}$$

$$\phi_{i,j,k}(s_{j,k}) + 2 s_{j,k} \phi_{i,j,k}(s_{j,k}) - (i + 2 mj + \frac{3}{2} k) \phi_{i,j,k}(s_{j,k})$$

$$= - \left\{ \sum_{f+i=1} e_f \phi_{i,f,j,k}(s_{j,k}) + \sum_{r+p=i} d_r \phi_{r,j,k-1}(s_{j,k}) + \frac{2}{3} (i + k - 3) \phi_{i,j,k-1}(s_{j,k}) \right\}$$

where

$$e_r = 2 (-1)^r s_r^f$$

$$d_r = \frac{2}{3} (-1)^r (r + 2) s_{r+1}^f$$

and the boundary value problem is given by

$$\sigma_{i,j,k}(s) = 0 \quad i, j, k \geq 0$$

$$\phi_{i,j,k}(s) = 0 \quad i, j, k \geq 0$$

$$s_0 = 0$$

$$\phi_{i,j,k}(0) = \sigma_{i,j,k}(0)$$

$$\sigma_{i,j,k}(0) = 0 \quad \text{unless } i = 0, j = 1, k = 2$$

$$\sigma_{0,1,2}(0) = c$$
If we take \( i = 0 \) in eqns. (A1)–(A8) (expanding plane electrode), the solutions obtained are shown in ref. 4.

If \( i = 1 \) (first-order spherical correction) we obtain

\[
\sigma_{1,1,i}(s_A) = 0 \quad \text{unless } j = 1, \ k = 3n + 2, \ n \geq 0
\]

\[
\sigma_{1,1,1}(s_A) = \frac{c^*}{2} \left( \psi_{m,1}(s_A) - \frac{6m + 4}{6m + 7} \psi_{m,7}(s_A) \right)
\]

\[
\sigma_{1,1,2}(s_A) = -\frac{c^*}{18} \left( 2(6m + 1) \psi_{m,-3}(s_A) - 12(3m + 2) \psi_{m,1}(s_A) + \frac{3(72m^2 + 168m + 89)}{6m + 7} \psi_{m,7}(s_A) - \frac{(6m + 10)(72m^2 + 240m + 155)}{(6m + 7)(6m + 13)} \psi_{m,13}(s_A) \right)
\]

\[
\sigma_{1,1,8}(s_A) = \frac{c^*}{648} \left( 6(6m + 1) \psi_{m,-11}(s_A) - (180m^2 + 768m + 81) \psi_{m,-1}(s_A) + (540m^2 + 1128m + 581) \psi_{m,1}(s_A) - (1296m^2 + 60048m + 88920m + 41292) \psi_{m,7}(s_A) + \frac{2(19440m^4 + 158976m^3 + 466344m^2 + 574560m + 247147)}{(6m + 7)(6m + 13)} \psi_{m,13}(s_A) - \frac{(7776m^4 + 78192m^3 + 274320m^2 + 388872m + 186014)(6m + 16)}{(6m + 7)(6m + 13)(6m + 19)} \times \psi_{m,19}(s_A) \right)
\]

Moreover,

\[
\phi_{1,1,i,k}^{+}(s_A) = \mp \gamma \phi_{1,1,i,k}^{+}(s_A) \quad \text{if } i = 2 \ 	ext{(second-order spherical correction)}
\]

If \( i = 2 \) (second-order spherical correction), we get

\[
\sigma_{2,1,1}(s_A) = 0 \quad \text{unless } j = 1, \ k = 3n + 2, \ n \geq 0
\]

\[
\sigma_{2,1,2}(s_A) = -\frac{c^*}{4} \left( p_{m,1} \psi_{m,-2}(s_A) - 2p_{m,1} \psi_{m,7}(s_A) + \frac{6m + 7}{6m + 10} p_{m,7} \psi_{m,10}(s_A) \right)
\]

\[
\sigma_{2,1,3}(s_A) = -\frac{c^*}{24} \left( \frac{2}{2(6m - 2)p_{m,1} \psi_{m,-8}(s_A) - 6(8m + 3)p_{m,1} \psi_{m,-2}(s_A)} + \frac{3(144m^2 + 252m + 112)}{6m + 4} p_{m,1} \psi_{m,1}(s_A) - \frac{2(864m^2 + 3564m^2 + 4716m + 1996)}{(6m + 7)(6m + 10)} p_{m,7} \psi_{m,10}(s_A) + \frac{(432m^2 + 2304m^2 + 3720m + 1836)}{(6m + 7)(6m + 19)} p_{m,19} \psi_{m,16}(s_A) \right)
\]

and

\[
\phi_{2,1,i,k}^{+}(s_A) = -\gamma \phi_{2,1,i,k}^{+}(s_A)
\]

In the preceding equations, when two signs appear, the upper one relates to a solution soluble product and the lower one to the amalgamation reaction. Moreover, superscripts “-” or “+” in the functions \( \sigma \) and \( \phi \) relate to the Koutecký function used, \( \psi_{m,v}^{+} \) or \( \psi_{m,v}^{-} \), respectively [18], where

\[
\psi_{m,v}^{+} = \psi_{(6m + v)/3}^{+}
\]

and

\[
p_{m,v} = p_{(6m + v)/3} = \frac{21}{6} \left( 1 + \frac{6m + v}{6} \right)
\]

where \( v \) is an integer value.

**NOTATION AND DEFINITIONS**

\( k_f, \ k_r \) heterogeneous rate constants of the forward and reverse charge-transfer reactions

\( k_s \) apparent heterogeneous rate constant of charge transfer at \( E^\circ \)

\( \tau \) blank period

\( t \) time elapsed between current application and measurement of the potential

\( t_e \) the blank period

\( A(t_e) \) time-dependent electrode area (\( = A_0 t_e^{2/3} \))

\( A_0 \) constant of proportionality of electrode area

\( r \) distance from the centre of electrode

\( r_0 \) electrode radius at time \( t_e \)

\( a \) (\( (3\pi n_{Hg}/4\pi d)^{1/3} \))

\( m_{Hg} \) rate of flow and density of mercury

\( \xi \) spherical correction parameter

\( \xi_{2,4} \) \( \xi_{2,4}/\sqrt{3} \)
$I(t)$  time-dependent faradaic current
$I_0$  constant applied rate of faradaic current increase
$E(t)$  time-dependent electrode potential
$\Gamma$  Euler gamma function

Other definitions are conventional.

REFERENCES