Cyclic voltammetry at constant sphericity

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Abstract

Cyclic voltammetry has been applied to the study of a simple charge transfer reaction at a spherical electrode such as the static mercury drop electrode. Theoretical and experimental curves have been obtained at constant sphericity both for a reversible and slow electrode process, taking into account amalgam formation. The use of constant sphericity lends great advantages since, on the one hand it allows us to discriminate between kinetic and curvature effects, and on the other reduces the interference from uncompensated IR drop. Methods for evaluating heterogeneous kinetic parameters are also proposed. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

For a long time cyclic voltammetry has been largely used for the elucidation of electrode processes as well as for the quantitative determination of the kinetic and thermodynamic parameters characteristic of a given electrode process. In spite of contributions to the study of cyclic voltammetry at spherical electrodes which have been carried out both for solution soluble product [1–3] and for amalgam formation [4–6], in practice experimentalists prefer to develop their investigations at plane electrodes, or at spherical ones when curvature effects have little importance, because when the time scale changes (the main tool for any kinetic study) it is difficult to discriminate between kinetic and curvature effects. However, it is evident that the apparent sphericity is given by the simultaneous contribution of the electrode radius and the time scale and, therefore, these contributions can be opposed and balanced.

In this paper we have used a purpose built static mercury electrode whose radius is easily modified (by changing the aperture time of a valve) in such a way that the apparent sphericity is held constant, by means of simultaneous actuation on the time scale and electrode radius. Moreover, with modern computer driven instrumentation (in which current–potential curves are stored in digital form) the transformation of experimental data to dimensionless curves is immediate. Thus, the simple visual inspection of a set of dimensionless curves at constant apparent sphericity (which behave qualitatively as those obtained for plane electrodes) allows us to investigate the mechanism of the electrode process and to evaluate the kinetic and thermodynamic parameters by means of a more detailed analysis. The use of this procedure gives additional advantages such as reducing the interference from uncompensated IR drop.

In turn, we have obtained theoretical curves at constant apparent sphericity for both a reversible and slow electrode process, taking into account amalgam formation. For numerical calculations we have used the Crank–Nicolson procedure, with implicit calculations of surface concentrations, and we have obtained working curves for the determination of kinetic parameters.

Finally, some experimental examples of the curves obtained at constant sphericity are given for systems in
which amalgamation takes place (because sphericity effects are more important for these systems), for both fast and slow electronic transfer.

2. Experimental

Data acquisition was performed using a DAS16-330-i (ComputerBoards, USA) board. All computer programs for data acquisition and data transformation were written in our laboratory. A computer driven potentiostat and sweep generator were designed and constructed by QUICELTRON (Spain). A static mercury drop electrode was constructed using a dropping mercury electrode (DME) EA 1019-1 (Metrohm) to which a purpose built valve was sealed. Depending on the DME used, the mercury pressure, and the open time for this valve, electrode radii in the range 0.01–0.05 cm have been obtained. For a given DME and mercury pressure the range has been slightly lower. A saturated calomel electrode and a platinum electrode were used as reference and auxiliary electrodes. Chemicals were analytical grade from Merck and were used as received. In all experiments the temperature was kept constant at 25 ± 0.2°C. Other methods and experimental conditions are described in [7].

In the case of reversible behavior, the values of diffusion coefficients have been calculated from peak currents. In 0.1 M KNO₃, we have obtained \( D_{\text{Cd}^{2+}} = 6.4 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1} \) and \( D_{\text{CdHg}0} = 1.6 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1} \), very close to those values found in the literature ([6,8,9]). Moreover, a value of \( E^0 = -0.575 \text{ V} \) has been assumed for the system \( \text{Cd}^{2+} | \text{Cd(Hg)} \). The same values were used in the presence of \( n \)-pentanol.

3. Theory

Mass transport to the electrode for the charge transfer reaction

\[
\text{A} + n \text{e}^- \rightarrow \text{B}
\]

is given by the following system of differential equations:

\[
\delta_A c_A = \delta_B c_B = 0
\]

where the linear differential operator \( \delta_i \) (\( i = \text{A, B} \)) for a spherical electrode such as the static mercury drop electrode, is given by

\[
\delta_i = \frac{\partial}{\partial t} - D_i \left( \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right)
\]

The boundary value problem associated with this process is defined by

\[
t = 0, \quad r \geq r_0 \quad \Rightarrow \quad c_A = c^a_A \quad (\text{S, A}) \\
t > 0, \quad r \rightarrow \infty \quad \Rightarrow \quad c_A = c^\infty_A \quad (\text{S}) \\
t = 0, \quad r \geq r_0 \quad \Rightarrow \quad c_B = c^a_B \quad (\text{S}) \\
t > 0, \quad r \rightarrow \infty \quad \Rightarrow \quad c_B = c^\infty_B \quad (\text{A}) \\
t = 0, \quad r \leq r_0 \quad \Rightarrow \quad \frac{\partial c_B}{\partial r} \bigg|_{r=0} = 0 \quad (\text{A}) \\
t > 0, \quad r = r_0 \quad \Rightarrow \quad \frac{\partial c_A}{\partial r} \bigg|_{r=r_0} = \mp \frac{\partial c_B}{\partial r} \bigg|_{r=r_0}
\]

\[
I(t) = k_A c_A(r_0, t) - k_B c_B(r_0, t)
\]

Eqs. (3), (4a), (5) and (6) are applied when the product is soluble in solution whereas Eqs. (3), (4b)--(6) define the conditions corresponding to the case of amalgamation formation. Note that in Eq. (5) two signs appear; the upper sign refers to a solution soluble product whereas the lower one refers to amalgam formation. (This convention is followed when two signs appear in the equations included in this paper).

Moreover, in Eq. (6) \( A \) is the electrode area and \( k_A \) and \( k_B \) are the heterogeneous rate constants of the forward and reverse transfer reactions, defined by

\[
k_A(E) = k_A \exp(-znF/RT(E - E^0))
\]

\[
k_B(E) = k_B \exp(((1 - x)nF/RT)(E - E^0))
\]

Note that both \( k_A \) and \( k_B \), which depend on the potential applied, are also a function of time for the case of cyclic voltammetry given by the relations

\[
0 \leq t \leq t_s; \quad E = E_0 - vt
\]

\[
t \geq t_s; \quad E = E_0 - 2\eta t_a + vt
\]

where \( E_0 \) is the initial potential, \( v \) is the potential sweep rate and \( t_s \) is the time at which the sweep is reversed.

For the purposes of simulation, it is appropriate to normalize the variables with the following expressions [10]

\[
C_i = c_i/c^a_A \quad (i = \text{A, B})
\]

\[
\Omega = t/t_R
\]

\[
R = r/\sqrt{(D_A t_R)}
\]

where \( t_R \) is a chosen experimental time-scale, which we have made coincident for convenience with the duration of the experiment. The diffusion equations are then

\[
\frac{\partial C_A}{\partial \Omega} = \frac{\partial^2 C_A}{\partial R^2} + \frac{2}{R} \frac{\partial C_A}{\partial R}
\]

\[
\frac{\partial C_B}{\partial \Omega} = \frac{1}{\gamma^2} \frac{\partial^2 C_B}{\partial R^2} + \frac{2}{R} \frac{\partial C_B}{\partial R}
\]

where
Fig. 1. Influence of sphericity on dimensionless voltammograms corresponding to a reversible charge transfer reaction. \( \gamma = 1 \). The values of \( R_0 \) are: (1) 0.75, (2) 1.25, (3) 1.75, (4) 2.5, (5) 10, (6) 100. (A) solution soluble product; (B) amalgamation of product.

\[
\gamma = \left( \frac{D_A}{D_B} \right)^{1/2}
\]
and the normalized boundary conditions become

\[
\Omega = 0, \quad R \geq R_0
\]
\[
\Omega > 0, \quad R \rightarrow \infty
\]
\[
\Omega = 0, \quad R \geq R_0 \quad C_A = C_B^* \quad (S, A)
\]
\[
\Omega > 0, \quad R \rightarrow \infty \quad C_B = C_B^* \quad (S)
\]
\[
\Omega = 0, \quad R \leq R_0 \quad C_B = C_B^* \quad (A)
\]
\[
\Omega > 0, \quad R = 0 \quad \left( \frac{\partial C_B}{\partial R} \right)_{R=0} = 0 \quad (A)
\]
\[
\Omega > 0, \quad R = R_0 \quad \frac{\partial C_A}{\partial R} = \frac{1}{\gamma^2 R_0} \frac{\partial C_B}{\partial R}
\]
\[
G = K_S(C_A(R_0, \Omega) e^{-\gamma^2} - C_B(R_0, \Omega) e^{1-\gamma^2})
\]

where the dimensionless variables \( G, K_S \) and \( \eta \) are given by

\[
G = \frac{I_R^2}{nFAD_A^2} \quad (20)
\]
\[
K_S = k_s \frac{1}{R_A^{1/2}} \quad (21)
\]
\[
\eta = (nF/RT)(E - E^0) \quad (22)
\]

Moreover, Eqs. (9a) and (9b) become

\[
0 \leq \Omega \leq \Omega^* \quad \eta = \eta_0 - \eta_M \Omega \quad (23a)
\]
\[
\Omega \geq \Omega^* \quad \eta = \eta_0 - 2\eta_M \Omega + \eta_M \Omega \quad (23b)
\]

where \( \eta_0 \) and \( \eta_M \) are, respectively, the dimensionless initial potential and the dimensionless potential sweep amplitude, with

\[
\eta_M = (nF/RT)M \quad (M: \text{potential sweep amplitude})
\]

Note that the dependence on the potential sweep rate \( \nu \) found in Eqs. (9a) and (9b) disappears in Eqs. (23a) and (23b) by using the above dimensionless variables Eqs. (11) and (24).

The digital simulation method considered is the Crank–Nicolson, for whose application we have also considered implicit calculations for surface concentrations [11]. The application of this method to this process is described in Appendix A, where we have also discussed the special case of amalgamation. Thus, we find the recursive relation given by Eq. (A9) in Appendix A, which allows us to carry out numerical calculations and to obtain theoretical curves both for the case in which the product is soluble at the electrolyte solution and for that corresponding to amalgamation formation.

4. Results and discussion

From digital simulation we obtain directly the dimensionless faradic flux at the electrode surface, \( G \), which is related to experimental variables through Eq. (20). However, it is more convenient to show experimental and calculated results by using the classical current function [2], denoted by \( \psi \). The relation between \( G, \psi \) and the experimental variables is given by

\[
\psi = \frac{G}{n} = \frac{I}{nFAD_A^2 c_A^*} \left( \frac{RT}{nFv} \right)^{1/2}
\]

For the sweep towards the negative direction we denote the corresponding current function with a subscript \( c \) as \( \psi_c \), and for the positive sweep with a subscript \( a \) as \( \psi_a \).

First of all, we refer to the theoretical curves obtained numerically by means of the Crank–Nicolson procedure (Figs. 1–6). For the purposes of simulation, the variables to take into account are \( \Omega, \eta_0, \eta_M, R_0, C_B^* \) and \( \gamma \). In addition, if the charge transfer reaction is slow it is necessary to refer to \( \alpha \) and \( K_S \). In this paper...
we will consider symmetric sweeps ($\Omega_s = 0.5$) and we assume that species B is initially absent ($C_{\text{ss}}^B = 0$).

Regarding the behavior of $\psi_c$ with the above variables, it is convenient to point out its obvious independence of $\eta_0$ if this variable reaches values sufficiently positive. On the other hand, owing to the definition of $R_{\text{op}}$ which includes the experimental time scale, $\psi_c$ depends on $\eta_M$ at a fixed value of $R_{\text{op}}$, although this dependence disappears when the product $R_{\text{op}}\eta_M^{1/2}$ remains constant. As can be expected, the value of the current function for the cathodic peak, $\psi_{\text{pc}}$, does depend on kinetic parameters of the charge transfer reaction. Its relative deviation from reversible behavior can be quantified by

$$\Delta\psi_{\text{pc}} = (\psi_{\text{pc(rev)}} - \psi_{\text{pc}})/\psi_{\text{pc(rev)}}$$  \hspace{1cm} (26)
the dimensionless anodic peak potential, $\eta_{pa}$, are practically independent of $\eta_p$.

According to the above discussion, for a reversible process the most significant variables are $R_0$ and $\gamma$. The dependence of $\psi$ on $R_0$ is shown in Fig. 1 in which we have included the two possible cases for the behavior of the reaction product: B is soluble in the electrolyte solution or B amalgamates into the electrode. As can be seen, $\psi_x$ is weakly dependent on the presence of amalgamation. Conversely, $\psi_a$ is strongly dependent on the behavior of the reaction product. Thus, when amalgamation takes place at the electrode, sphericity effects are much more important. The main aim of this paper is to show how to take advantages of sphericity in kinetic studies. In turn, some papers deal with cyclic voltammetry with slow charge transfer at spherical electrodes with a solution soluble product [2,3], while as far as we know, slow charge transfer with amalgamation has not been studied yet. Thus, our attention will be focused in the study of amalgamation and we refer to this situation below.

The effect of $\gamma$ on the $\psi-\eta$ curves is shown in Fig. 2. As noted, the dependence of $\psi_a$ on $\gamma$ is very marked in such a way that it can be used for purposes of determination.

For a slow charge transfer reaction, the kinetic parameters markedly influence the $\psi-\eta$ response. Fig. 3 illustrates the dependence of the $\psi-\eta$ curves on the kinetic variables $x$ and $K_b$ for a fixed value of $R_0$. Under these conditions (fixed value of $R_0$) the behavior of these curves is qualitatively very close to that found for a plane electrode [12,13]. In experimental studies it is very easy to generate different values of $K_b$ by simply changing the sweep rate. Thus, it is convenient to design working curves in order to determine $K_b$ from experimental measurements, by keeping constant all other necessary variables. $K_b$ and $x$ affect the characteristics of the peaks (position, width, relative intensity), but they are not the only determining factors (for example, sphericity also strongly influences these characteristics). In order to minimize other non-kinetic influences the measurements refer to a reversible charge transfer reaction. Thus, in order to make the working curves we have selected the following four variables (which can be obtained experimentally):

1. $\Delta\psi_{pc}$
2. $\Delta\psi_{pa}$
3. The absolute value of the difference between the anodic and cathodic peak potentials, relative to a reversible process, given by

$$\Delta\eta_p = |(\eta_{pc} - \eta_{pa}) - (\eta_{pc(rev)} - \eta_{pa(rev)})|$$

where $\eta_{pc}$ is the dimensionless cathodic peak potential, $\eta_{pa}$ is the anodic one, and $\eta_{pc(rev)}$ and $\eta_{pa(rev)}$ are the respective values corresponding to a reversible process.

---

Fig. 5. Influence of sphericity on the working curves obtained for $x = 0.5$. The values of $R_0$ are: (1) 1, (2) 2, (3) 5, (4) 10. Other conditions as in Fig. 4.

$$\Delta\psi_{pa} = (\psi_{pa(rev)} - \psi_{pa})/\psi_{pc(rev)}$$

(27)

For the evaluation of $\Delta\psi_{pa}$, it is not necessary to use any arbitrary base line if values of $\psi_{pa(rev)}$ and $\psi_{pc(rev)}$ are available (these values can be obtained from experimental measurements or can be easily calculated). Moreover, if the cathodic peak is well developed, $\Delta\psi_{pa}$ and

Fig. 6. Effects of $\gamma$ on the working curves obtained for $x = 0.5$. The values of $\gamma$ are: (1) 0.6, (2) 1, (3) 1.4. Other conditions as in Fig. 4.
4. The cathodic peak width relative to a reversible process, given by

$$\Delta \eta_{p/2} = |(\eta_{pc} - \eta_{pc2}) - (\eta_{pc2(\text{rev})} - \eta_{pc2(\text{rev})})|$$

(29)

where $\eta_{pc2}$ is the dimensionless cathodic half-peak potential and $\eta_{pc2(\text{rev})}$ the respective value corresponding to a reversible process.

In Fig. 4 we have plotted an example of these working curves obtained for different values of $\alpha$. Strictly, we must know the $\alpha$-value to use these curves. However, if we do not know $\alpha$, we can proceed in the following way: first we can estimate $\alpha$ from the values of $\Delta \eta_{p/2}$ which is very sensitive to the $\alpha$-values. With the estimated value of $\alpha$ we select the appropriate working curve for $\Delta \psi_{pc}$ and $\Delta \psi_{pa}$. If the selected $\alpha$-value is larger than the true one, the values obtained for $K_\alpha$ from $\Delta \psi_{pc}$ will be systematically higher than those obtained from $\Delta \psi_{pa}$. Conversely, if the selected $\alpha$-value is smaller than the true one the opposite situation will occur. In turn, the values of $K_\alpha$ obtained from $\Delta \eta_{p}$ (with a smaller dependence on $\alpha$) generally take intermediate values between both situations. Thus, by a very simple and systematic trial and error procedure, accurate values of $\alpha$ and $K_\alpha$ (or $K_\beta$) can be obtained.

When a kinetic study is carried out it is necessary to know all the other non-kinetic parameters in order to use the working curves from Fig. 4. In this case these parameters are mainly $R_0$ and $\gamma$. In Figs. 5 and 6 we have plotted the working curves obtained for different values of $R_0$ (Fig. 5) and $\gamma$ (Fig. 6). Note that the working curves corresponding to the dimensionless potentials or to the current function of the cathodic peak are weakly influenced by $R_0$ and $\gamma$ (this is due to the fact that the experimental variables in the working curves refer to a reversible process), whereas $\Delta \psi_{pa}$ depends strongly on $R_0$ and $\gamma$. Thus, very accurate values of $R_0$ and $\gamma$ are needed if the current function corresponding to the anodic peak is used for kinetic determinations.

5. Experimental results

The time scale in cyclic voltammetry is determined by the sweep rate. Hence, the immediate procedure to study the influence of the time scale in a given electrode process consists in carrying out a set of voltammetric experiments at different sweep rates, using the same electrode at a fixed value of its radius, $r_0$. This is equivalent to a set of experiments in which the variable is $R_0$. Consequently, one can expect results comparable to those found in Fig. 1 if one calculates the current function corresponding to this set of experiments when the charge transfer reaction is reversible. According to this, in Fig. 7, we have plotted cyclic voltammograms at different sweep rates (ranging from 100 to 10 mV s$^{-1}$) corresponding to a 1 mM Cd$^{2+}$ in 0.1 M KNO$_3$ solutions. Owing to the presence of amalgamation, a very important sphericity effect is shown. However, for a reversible process it is evident that the current function obtained in a experimental series in which $R_0$ remains constant must give rise to a set of superposed curves, even when the sweep rate changes. In order to keep $R_0$ constant in this experimental series carried out at different values of the sweep rate, we must modify the electrode radius, $r_0$, in such a way that the product $r_0^2$ remains constant. By using two electrodes or by changing the mercury pressure we have obtained changes in electrode radius of a factor equal to 5 (for example in the range 0.01–0.05 cm), hence the sweep rate can be modified by a factor of 25. However, in practice, the use of only one electrode and no change in mercury pressure is preferred. Under these conditions, if the electrode radius can be modified by a factor equal to 3 (for example in the range 0.01–0.03 cm) a near 10-fold increase in sweep rate is available for a given value of $R_0$. Apparently this restriction constrains the applicability of the method. However, constant sphericity voltammograms can be 'stepped' to cover a very wide time scale. Hence, we must select a set of electrode radii and apply the condition of constant sphericity for several values of $R_0$. For example, we can select an $R_0$-value of 1 to cover the sweep rate range of 10–100 mV s$^{-1}$, an $R_0$-value of 3.2 for the range 100–1000 mV s$^{-1}$, an $R_0$-value of 10 for the range 1000–10000 mV s$^{-1}$, etc. In this way the more interesting time scale region, for kinetic purposes, can be studied at constant sphericity.

Experimental curves obtained at fixed $R_0$ and conditions very close to those shown in Fig. 7 (scan rates ranging from 125 to 11.5 mV s$^{-1}$) are shown in Fig. 8.
The kinetic characteristics of the reduction of Cd$^{2+}$ in the presence of $n$-pentanol are evident by simple visual inspection. We have obtained from this figure $k_s = 1.8 (\pm 0.05) \times 10^{-3}$ cm s$^{-1}$ and $\alpha = 0.60 \pm 0.02$ by using the trial and error procedure described above.

Figs. 8 and 9 have been obtained for $R_\sigma$ values close to 2, for which sphericity effects are important if amalgamation takes place. It is evident that under these conditions it is very convenient to work at constant sphericity (that is to say, at fixed values of $R_\sigma$). However, there is less evidence for the convenience of working at constant sphericity if $R_\sigma$ takes larger values. There is one important reason to work at constant sphericity with large $R_\sigma$ values: the smaller uncompensated $IR$ drop effects.

If the double layer capacitance does not depend on potential, the double layer charging current is proportional to $R_\sigma e$. Therefore, in a set of experiments carried out at constant sphericity the charging current should remain constant in all of them. The uncompensated $IR$ drop effects become obviously more appreciable as the total current flux through the cell increases. For fixed area electrodes and simple charge transfer reactions the total (faradaic and charging) current increases as the sweep rate does. Thus, $IR$ drop effects are always more appreciable at higher sweep rates and can be confused with those caused by a slow charge transfer reaction [14]. However, for experiments corresponding to a simple fast charge transfer reaction carried out at constant sphericity, the total current decreases as the sweep rate increases. In fact the charge current remains constant, as discussed above, and the faradaic current decreases.

The decrease in the faradaic current is due to the fact that the value of $\psi$ does not change from one experiment to another and therefore, according to Eq. (25) the product $R_\sigma^{1/2}$ for a given point of the $\psi - E$ curve remains constant in all the experiments. Consequently, $IR$ drop effects are less appreciable at high sweep rates and must not be confused with kinetic effects.

In Figs. 10 and 11 we have plotted the current function for experiments carried out at constant sphericity for fast (Fig. 10) and slow (Fig. 11) charge transfer reactions for large $R_\sigma$ values and sweep rates ranging from 2000 to 225 mV s$^{-1}$. The superposition of the $\psi - E$ curves noted for a reversible process reveals no appreciable double layer or $IR$ effects under these conditions. Thus, we can be sure that the behavior shown in Fig. 11 is merely due to a slow charge transfer reaction. Moreover, we have obtained from these curves the values of $k_s = 1.1 (\pm 0.05) \times 10^{-2}$ and $\alpha = 0.64 \pm 0.2$.

In short, we have shown that the $\psi - E$ curves obtained at constant sphericity for a simple charge transfer reaction behave qualitatively as those corresponding to a plane electrode. Similar behavior can be expected of other more complex reaction mechanisms. In this...
Fig. 10. Experimental $\psi - E$ response for a 1 mM Cd$^{2+}$ solution in 0.1 M KNO$_3$. $r_0^{1/2} = 0.720$ cm mV$^{1/2}$ s$^{-1/2}$. The experiments have been carried out for the following values of $v$ (mV s$^{-1}$): 225, 471, 764, 1100, 2000.

Fig. 11. Experimental $\psi - E$ curves for a 1 mM Cd$^{2+}$ solution in 0.1 M KNO$_3$ and 0.066 M in n-pentanol. $r_0^{1/2} = 0.72$ cm mV$^{1/2}$ s$^{-1/2}$. The experiments have been carried out at the following values of $v$ (mV s$^{-1}$): (1) 225, (2) 471, (3) 764, (4) 1100, (5) 2000. The respective curve obtained in the absence of n-pentanol for $v = 225$ mV s$^{-1}$ (curve 6) has been also included.

way cyclic voltammetry at constant sphericity can be a powerful tool for the diagnosis of many reaction mechanisms at mercury electrodes. IR drop effects are not eliminated but its effects are in some degree reduced by using constant sphericity.

6. Nomenclature

$A$ electrode area

c$^i$, $c_i^*$ concentration of species $i$ ($i = A, B$)
bulk concentration of species $i$
dimensionless concentration of species $i$
$C_i^*$ dimensionless bulk concentration of species $i$
$E^o$ formal potential of the electrode reaction
$E_0$ initial potential applied to the electrode
g dimensionless current $(nFAD_i^{1/2}/(nFAD_i^{1/2})$
c$^*_{\lambda}$)
h$^k$ dimensionless space interval ($k = A, B$)
k$_r$, k$_b$ heterogeneous rate constants of the forward and reverse charge transfer reactions
k$_S$ standard rate constant of an electrode reaction
K$_S$ dimensionless standard rate constant of an electrode reaction ($k_S_l_0^2/D_\lambda^{1/2}$)
M potential sweep amplitude
distance from the center of the electrode
r$_0$ electrode radius for a static mercury drop electrode
R$_0$ dimensionless variable corresponding to the distance from the center of the electrode ($r_r(D_r t_r)^{1/2}$)
r dimensionless electrode radius
t time elapsed between the application of the potential and the current measurement
t$_s$, t$_R$ time at which the sweep is reversed experimental time-scale coincident with the duration of the experiment ($M/v$)
v potential sweep rate

Greek letters

$\alpha$ electron transfer coefficient
$\gamma$ $(D_A/D_B)^{1/2}$
$\lambda^k$ dimensionless time interval
$\eta$ dimensionless potential ($nF(E-E^o)/$ (RT))
$\eta_0$ dimensionless initial potential
$\eta_M$ dimensionless potential sweep amplitude
$\eta_{pc/2}$ dimensionless cathodic half-peak potential
$\eta_{pc/2(rev)}$ dimensionless cathodic half-peak potential corresponding to a reversible process
$\eta_{pc}$, $\eta_{pa}$ dimensionless cathodic and anodic peak potentials
\[ \Delta \eta_S = \frac{(\eta_{pc} - \eta_{pa}) - (\eta_{pc(rev)} - \eta_{pa(rev)})}{G \eta_M} \]
\[ \Delta \eta_{S/2} = \frac{(\eta_{pc} - \eta_{pa}) - (\eta_{pc(rev)} - \eta_{pa(rev)})}{G \eta_M} \]
\[ \Delta \psi_{pc} = \left( \psi_{pc(rev)} - \psi_{pc} \right) / \psi_{pc(rev)} \]
\[ \Delta \psi_{pa} = \left( \psi_{pa(rev)} - \psi_{pa} \right) / \psi_{pa(rev)} \]
\[ \psi = \text{current function} \ (G \eta_M) \]
\[ \psi_{pc}, \psi_{pa} = \text{cathodic and anodic current functions} \]
\[ \psi_{pc(rev)}, \psi_{pa(rev)} = \text{cathodic and anodic current functions corresponding to the cathodic and anodic peaks} \]
\[ \psi_{pc(rev)} \text{ of electrons corresponding to the cathodic and anodic peaks for a reversible process} \]
\[ \Omega = \text{dimensionless time} \ (t / \tau_p) \]
\[ \Omega_a = \text{dimensionless time at which sweep is reversed} \]

Other symbols are conventional.

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Appendix A

By using the Crank-Nicolson procedure, the diffusion (Eqs. (13) and (14)) with \( \Omega = \delta \Omega \), \( R = R_0 + ih \), and \( R = R_0 \pm ih \), may be discretized as follows

\[ a_i^k C_j^{i+1} + b_i^k C_j^{i+1} + d_i^{k+1} C_j^{i+1} = e_i^{k+1} \]

where

\[ a_i^k = 1 - \frac{h^k}{R_0 + ih^k} \]
\[ b_i^k = 1 + \frac{h^k}{R_0 - ih^k} \]
\[ d_i^{k+1} = -2 \frac{\lambda^k + 1}{\alpha^k + 1} \]
\[ e_i^{k+1} = 1 + \frac{h^k}{R_0 + ih^k} \]

with

\[ \lambda^k = \frac{d \Omega}{(h \delta)^2} \]

\[ C_{j_{max}}^k = C_{j_{max}}^{k+1} \]

\[ C_{j_{max}}^{k+1} = C_{j_{max}}^k \]

\[ C_{j_{max}}^{k+1} = C_{j_{max}}^k \]

Eqs. (A7) and (A8a) are applied when the product is soluble in solution, and Eqs. (A7) and (A8b) for the case of amalgam formation. Eq. (A8b) is deduced from the boundary condition (Eq. (17c)), which has been discretized by using the two-point approximation.

The tridiagonal system of Eq. (A1) may become bidiagonal if we take into account the values of \( d_i^{k+1} \) and \( C_{j_{max}}^k \) given by Eqs. (A7), (A8a) and (A8b), and we start with the last equations of this system by carrying out a reiterative procedure. Thus, we obtain the following recursive relation

\[ a_i^{k+1} C_j^{i+1} + b_i^{k+1} C_j^{i+1} + d_i^{k+1} C_j^{i+1} = e_i^{k+1} \]

where the new coefficients which appear are given by

\[ b_i^{k+1} = b_i^k - \frac{a_i^{k+1} d_i^{k+1}}{b_i^{k+1}} \]

\[ e_i^{k+1} = e_i^k - \frac{d_i^{k+1} e_i^{k+1}}{b_i^{k+1}} \]

Moreover, for the case of solution soluble product we find

\[ b_i^{k+1} = b_i^k \]

\[ e_i^{k+1} = e_i^{k+1} - d_i^{k+1} C_k^{i+1} \]

whereas for the case of amalgamation we obtain

\[ b_i^{k+1} = b_i^k \]

\[ e_i^{k+1} = e_i^{k+1} - d_i^{k+1} C_k^{i+1} \]

In our numerical calculations carried out by using Eq. (A9)–Eq. (A13) or Eqs. (A14a), (A14b), (A15a) and (A15b) and Eq. (A2a)–Eq. (A6) we have taken the same number of points for both reduced and oxidized species concentration profiles (i.e. \( i_{max} \) takes the same value for both species) and we have also made the following assumptions:
(a) When both reduced and oxidized species are soluble in solution we have assumed $i_{max}^{A} = i_{max}^{B} = 6$.

(b) When amalgamation of product takes place at the electrode we have distinguished between the two following cases, according to the value of $R_o$:

- (b-1) $R_o < 6$. In this case we have assumed $i_{max}^{A} = 6$ and $i_{max}^{B} = R_o$.

- (b-2) $R_o > 6$. Under these conditions, the assumption $i_{max}^{A} = i_{max}^{B} = 6$ has been made and the Koutecký approximation [15], which neglects the finite volume of the electrode, has been applied successfully. The application of this approximation leads to Eqs. (A12) and (A13) for $i_{max}^{A}$, instead of Eq. (A14a)–Eq. (A15b), where the coefficients which appear for $k = B$ are given by Eqs. (A3b), (A4b) and (A5b) with the appropriate sign corresponding to amalgam formation. We have also verified, under these conditions, that the errors found by using the Koutecký approximation are lower than 0.3% for the anodic peak current and than 0.01n mV for the anodic peak potential.

The boundary conditions (Eqs. (18) and (19)) may be discretized as follows

$$G = \frac{-25C_{-1.0}^{A} + 48C_{-1.1}^{A} - 36C_{-1.2}^{A} + 16C_{-1.3}^{A} - 3C_{-1.4}^{A}}{12h^{A}}$$

$$= -\frac{1}{\gamma^{2}}$$

$$\left(\frac{-25C_{-1.0}^{B} + 48C_{-1.1}^{B} - 36C_{-1.2}^{B} + 16C_{-1.3}^{B} - 3C_{-1.4}^{B}}{12h^{B}}\right)$$

\[ (A16) \]

if we use the 5-point approximation for the individual concentration gradients at the electrode.

For the implicit calculation of surface concentrations we need to solve a system of 11 equations, which correspond to the first four equations of the system (Eq. (A9)) (for $k = A$ and $k = B$), besides the three equations corresponding to the conditions in Eq. (A16) and Eq. (A17).

References