

REGENERATION MECHANISM STUDIED BY POTENTIAL–TIME RESPONSE TO SINUSOIDAL CURRENT–TIME FUNCTION

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A theoretical study of the potential–time response to sinusoidal current applied to static and dynamic electrodes for regeneration processes is presented. Methods for determination of the regeneration fraction, rate constant of the chemical reaction and heterogeneous kinetic parameters are proposed.

Key words: Electrochemistry; Chronopotentiometry; Homogeneous kinetics; Static mercury drop electrode.

In our two previous papers^{1,2}, we have shown the importance of an alternating current chronopotentiometry as a tool for investigation of reaction mechanism. The AC current perturbation allows us to record the potential–time curve of the reoxidation process under conditions when the oxidized species is not depleted at the electrode surface. In contrast to DC programmed current³ it provides an additional information on the electrode kinetics when both reduction and oxidation transition times can be used.

A sinusoidal current perturbation $I(t) = I_0 \sin(\omega t)$ is applied to various types of electrodes – dropping mercury electrode (DME), static mercury drop electrode (SMDE) and a plane electrode. For a DME the more rigorous model of an expanding sphere is considered assuming advantageously the existence of a blank period $t_1 \geq 0$ (ref.⁴). The response of a static mercury drop electrode and a plane electrode can be derived from transformed DME equations.

Although the treatment described in this paper is valid for any number of cycles of the alternating current, it is more convenient to use only its first cycle since the transition time of oxidized or reduced species is always reached during the first cycle (before or after the current changes its sign, respectively).

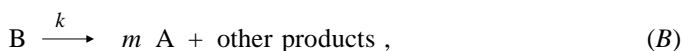
The dependence of the potential–time curves and of the reduction and oxidation transition times on the homogeneous rate constant and on the regeneration fraction is discussed for different regeneration mechanisms.

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Finally, we propose methods for determination of the regeneration fraction, the rate constant of the chemical reaction, as well as kinetic parameters of the heterogeneous reaction.

THEORETICAL

For a regeneration mechanism, represented by the Eqs (A) and (B)



where k_{red} and k_{ox} are the rate constants of forward and reverse reactions (A), the stoichiometric coefficient a and b correspond to the cathodic and anodic reaction orders, k is the first-order rate constant of the chemical reaction and coefficient m may have any positive value. The associated boundary value problem is given by⁵

$$\left. \begin{aligned} \hat{\delta}_A C_A &= mkC_B \\ \hat{\delta}_B C_B &= -kC_B \end{aligned} \right\} \quad (1)$$

$$\left. \begin{aligned} t=0, \quad r > r_0 \\ t > 0, \quad r \rightarrow \infty \end{aligned} \right\} : C_A = C_A^* ; C_B = 0 \quad (2)$$

$$t > 0, \quad r = r_0 :$$

$$\frac{D_A}{a} \left(\frac{\partial C_A}{\partial r} \right)_{r_0} = - \frac{D_B}{b} \left(\frac{\partial C_B}{\partial r} \right)_{r_0} = \frac{I(t)}{nFA(t_s)} . \quad (3)$$

Moreover,

$$\frac{I(t)}{nFA(t_s)} = k_{\text{red}} C_A^a(r_0, t) - k_{\text{ox}} C_B^b(r_0, t) , \quad (4)$$

where $\hat{\delta}_i$ is the operator corresponding to the expanding sphere⁶

$$\hat{\delta}_i = \frac{\partial}{\partial t} - D_i \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) + \frac{\zeta^3}{3r^2} \frac{\partial}{\partial r} \quad (5)$$

and k_{red} and k_{ox} are given by^{7,8}

$$k_{\text{red}} = k_{\text{c}}^0 \exp \left\{ \frac{-\alpha n F}{\nu R T} [E(t) - E_{\text{c}}^{0'}] \right\} \quad (6)$$

$$k_{\text{ox}} = k_{\text{c}}^0 \exp \left\{ \frac{\alpha' n F}{\nu R T} [E(t) - E_{\text{c}}^{0'}] \right\}, \quad (7)$$

where $E_{\text{c}}^{0'}$ is the formal potential of the electrode reaction and k_{c}^0 is the corresponding rate constant. We assume that the charge transfer reaction remains rate-controlling over the wide range of potentials involved (*i.e.* $\alpha' = 1 - \alpha$) and that the stoichiometric number $\nu = 1$.

When an alternating current of the form

$$I(t) = I_0 \sin(\omega t) \quad (8)$$

is applied to a DME, the above problem may be solved by introducing the variables

$$\left. \begin{aligned} \zeta &= C_{\text{B}} + \frac{C_{\text{A}}}{m} \\ \phi &= C_{\text{B}} e^{kt} \end{aligned} \right\} \quad (9)$$

and proceeding as in refs^{1,9}. Thus, if we assume

$$D_{\text{A}} = D_{\text{B}} = D \quad (10)$$

we find that the surface concentrations of electroactive species are given by

$$\frac{C_{\text{A}}(r_0, t)}{C_{\text{A}}^*} = 1 - a N_{\text{DME}} t^{1/2} [(1-p)S + pX] \quad (11)$$

$$\frac{C_{\text{B}}(r_0, t)}{C_{\text{A}}^*} = b N_{\text{DME}} t^{1/2} X, \quad (12)$$

where

$$N_{\text{DME}} = \frac{2I_0}{nF A(t_s)D^{1/2}C_A^*} \quad (13)$$

$$A(t_s) = A_0 t_s^{2/3} \quad (14)$$

$$t_s = t_1 + t \quad (15)$$

and the regeneration fraction p is defined by

$$p = \frac{mb}{a} \quad (16)$$

In Eq. (15), t_1 is a time delay prior to application of the current and S and X in Eqs (11) and (12) are functional series defined in Appendix, Eqs (A1)–(A6).

For a static mercury drop electrode, N_{DME} is transformed to N_{SMDE} according to Eq. (A13), which becomes time-independent. Moreover, the S and X series in Eqs (11) and (12) for an SMDE are simplified to Eqs (A14) and (A15) in Appendix.

When I_0 and/or ω in Eq. (8) take values corresponding to $C_A \rightarrow 0$ at the electrode surface before the current changes its sign, the reduction transition time, τ_A , is reached. At this moment the experiment is stopped⁴ to avoid decomposition of supporting electrolyte. Thus, by setting $C_A = 0$ in Eq. (11), we obtain

$$\tau_A^{1/2} = \frac{(t_1 + \tau_A)^{2/3} nF A_0 D^{1/2} C_A^*}{2aI_0 [(1-p)S + pX]_{t=\tau_A}}, \quad (17)$$

where $\chi = kt$ and X is a power series of the rate constant of the chemical reaction. For asymptotic solution see Appendix, Eq. (A11).

If the current density is not high enough to reach τ_A , the depletion of species B at the electrode surface takes place after the current changes its sign and τ_B is always reached. Under these conditions we obtain

$$[X]_{t=\tau_B} = 0 \quad (18)$$

by setting $C_B = 0$ in Eq. (12). Here τ_B is the value of t for which the functional series X is equal to zero. Note that τ_B does not depend on most of the experimental parameters (*i.e.* I_0 , C_A^* , A_0), whereas τ_A does.

Since the X series included in Eqs (17) and (18) contains all information about the rate of the chemical step of the electrode process, both reduction and oxidation transition times depend on the kinetics of the chemical step and therefore may be used for determination of the homogeneous rate constant k (see Results and Discussion).

The general expression for the potential–time response can be obtained by including Eqs (11) and (12) in Eq. (4). Thus, we find

$$\frac{N_{\text{DME}} D^{1/2}}{2k_s} \sin(\omega t) e^{\alpha\eta(t)} = (C_A^*)^{a-1} \left\{ 1 - aN_{\text{DME}} t^{1/2} [(1-p)S + pX] \right\}^a - e^{\eta(t)} (C_A^*)^{b-1} \left\{ bN_{\text{DME}} t^{1/2} X \right\}^b, \quad (19)$$

where

$$\eta(t) = \frac{nF}{RT} (E(t) - E_c^0). \quad (20)$$

Note, that according to Eq. (19), the $E-t$ curves depend on the concentration of species A if $N_{\text{DME}} t_s^{2/3}$ (Eq. (13)) is fixed and the reaction orders a and b are different from unity.

For a reversible process, Eq. (19) is simplified to

$$E(t) = E_c^0 + \frac{RT}{nF} \ln \frac{(C_A^*)^{a-b} \left\{ 1 - aN_{\text{DME}} t^{1/2} [(1-p)S + pX] \right\}^a}{\left\{ bN_{\text{DME}} t^{1/2} X \right\}^b}. \quad (21)$$

This equation may be written in the form

$$E(t) = E_{1/2}^r + \frac{RT}{nF} \ln \frac{2^{a-b} \left\{ 1 - aN_{\text{DME}} t^{1/2} [(1-p)S + pX] \right\}^a}{\left\{ aN_{\text{DME}} t^{1/2} X \right\}^b}, \quad (22)$$

where $E_{1/2}^r$ is the reversible polarographic half-wave potential given by¹⁰

$$E_{1/2}^r = E_c^0 + \frac{RT}{nF} \ln \left\{ \left(\frac{a}{b} \right)^b \left(\frac{2}{C_A^*} \right)^{b-a} \right\}. \quad (23)$$

As can be noted from Eqs (21)–(23), the $E-t$ curves obtained for a reversible process depend on C_A^* if $N_{\text{DME}} t_s^{2/3}$ is fixed and the reaction orders a and b are not equal. Conversely, when $a = b$, Eq. (21) becomes concentration-independent.

Totally Irreversible Process

The following two cases can be described:

1. At condition $I(t) > 0$ ($\omega t < \pi$), Eq. (19) is transformed to

$$E(t) = E_c^{0'} + \frac{RT}{\alpha nF} \ln \frac{2k_s (C_A^*)^{a-1}}{N_{\text{DME}} D^{1/2}} + \frac{RT}{\alpha nF} \ln g_C, \quad (24)$$

where

$$g_C = \frac{\{1 - aN_{\text{DME}}t^{1/2} [(1-p)S + pX]\}^a}{\sin(\omega t)}. \quad (25)$$

2. At condition $I(t) < 0$ ($\pi < \omega t < 2\pi$), Eq. (19) becomes

$$E(t) = E^0 - \frac{RT}{(1-\alpha)nF} \ln \frac{2k_s (C_A^*)^{b-1}}{N_{\text{DME}} D^{1/2}} + \frac{RT}{(1-\alpha)nF} \ln g_A, \quad (26)$$

where

$$g_A = \frac{-\sin(\omega t)}{\{bN_{\text{DME}}t^{1/2}X\}^b}. \quad (27)$$

Moreover, as follows from Eqs (19)–(21) and (24)–(27), the potential–time response obtained for this mechanism is always affected by the kinetics of the chemical step. It does not depend on the degree of irreversibility of the charge transfer reaction, since both A and B species involved in the electrode process take part in the chemical step.

RESULTS AND DISCUSSION

Equations presented in this paper are valid for any value of the regeneration fraction p .

General Cases

1. For $p = 0$, $m = 0$ (see Eq. (16)). The reaction scheme is simplified either to an EC mechanism (discussed in ref.²) or to a charge transfer reaction (E process) for $k = 0$, $\chi = 0$ (Eq. (A8)).

2. For $0 < p < 1$, $m < a/b$ and the regeneration of species A is only partial. As an example we can mention the regeneration half reaction for which $p = 0.5$, in the reduction of oxygen on mercury in presence of catalase^{11,12}.

3. The value $p = 1$ corresponds to a total regeneration of species A, *i.e.* $m = a/b$, refs^{13,14} and the response for this mechanism is influenced by the X series (Eq. (11)). Detailed study of a catalytic mechanism with $a = b = m = 1$ is published in ref.¹⁵.

4. For $p > 1$, $h > a/b$ and the regeneration of A exceed its starting level. An illustrative example is the reduction of iodine in the presence of iodate on a platinum electrode, where $p = 1.2$ (refs^{11,16}).

The particular cases 2, 3 and 4 will be considered below.

Transition Times

As mentioned above, the transition time of the oxidized species is reached when $C_A(r_0, \tau_A) = 0$. For this condition, the value of $N_{\text{DME}} t_s^{2/3}$ given by Eq. (13) must be higher than a fixed minimum value N_{min} (ref.⁴) given by Eqs (11), (13) and (14)

$$N_{\text{min}} = \left(\frac{2I_0}{nFA_0D^{1/2}C_A^*} \right)_{\text{min}} = \frac{1}{aH_{\text{max}}}, \quad (28)$$

where H_{max} is the absolute maximum of the time function of H defined as

$$H = [(1-p)S + pX] \frac{t^{1/2}}{t_s^{2/3}}. \quad (29)$$

Note that N_{min} depends on both the regeneration fraction p and the rate constant k (X series) as well as on the frequency of the alternating current ω (S and X series).

When the current density is not high enough for the depletion of species A, τ_B is always reached (after the current changes its sign) independently of the value of regeneration fraction p . This behaviour is of great advantage in practice since it allows us to work always under conditions at which τ_A or τ_B is reached. In this way, a relevant kinetic information may be obtained from τ_A and τ_B due to their dependence on the kinetics of the chemical step (see Eqs (17) and (18)). Although both τ_A and τ_B can be used for determining the rate constant k of the chemical reaction, it is more convenient to use the oxidation transition time τ_B . It is independent of most experimental parameters (*i.e.* I_0 , C_A^* and electrode area) and of the regeneration fraction value p , in contrast to τ_A . In order to determine the rate constant k from τ_A , the regeneration fraction value must be known, according to Eq. (17).

The rate constant k can easily be found from Fig. 1. The theoretical curves have been obtained under conditions when A is not depleted at the electrode surface. The features of the theoretical curves in Fig. 1 are identical to those found for a CEC process¹. They coincide with curves obtained for CEC and EC mechanisms with an irreversible chemical step.

Once k is known, the regeneration fraction p can be found from τ_A using the theoretical curves in Fig. 2, for several values of p . These curves were obtained from Eq. (17) when the transition time of species A is reached. Thus, we find

$$Y\left(\frac{\tau_A}{\tau_A^c}\right)^{1/2} = \frac{1}{(1-p) + p(X/S)_{t=\tau_A}}, \quad (30)$$

where

$$Y = \left(\frac{t_1 + \tau_A^c}{t_1 + \tau_A}\right)^{2/3} \frac{(S)_{t=\tau_A}}{(S)_{t=\tau_A^{(c)}}}. \quad (31)$$

It is interesting to note the different behaviour of curves plotted in Fig. 2 for $p < 1$ and $p \geq 1$. When $p < 1$, $Y(\tau_A/\tau_A^c)^{1/2}$ increases with χ_{τ_A} towards its asymptotic value $1/(1-p)$, according to Eqs (30) and (A11).

Conversely, for $p \geq 1$, $Y(\tau_A/\tau_A^c)^{1/2}$ increases continuously with χ_{τ_A} , although its rise for $p > 1$ is faster than for $p = 1$. Note that for $p > 1$, τ_A exists only for those values of p which satisfy the following condition (see (Eq. (30))

$$\frac{p}{p-1} > \left(\frac{S}{X}\right)_{t=\tau_A}. \quad (32)$$

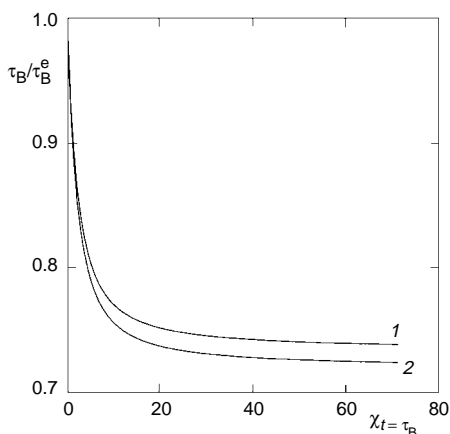


FIG. 1
Curves τ_B/τ_B^e vs $\chi_{t=\tau_B}$ deduced from Eq. (18) for a DME; $\xi = 0$, $\Omega_1 = 3$ (1), $\Omega_1 = 0$ (2)

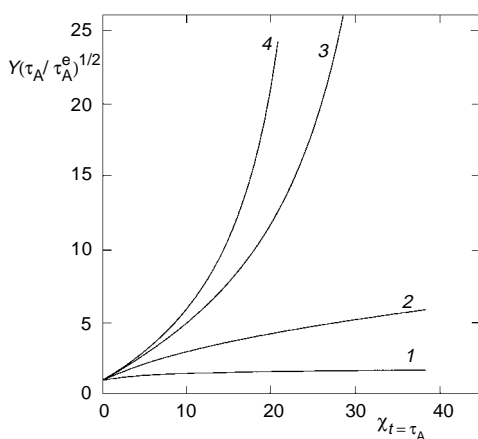


FIG. 2
Dependence of $Y(\tau_A/\tau_A^e)^{1/2}$ on $\chi_{t=\tau_A}$ for an SMDE from Eqs (30) and (A19), $\xi_{t=\tau_A} = 0.2$, $\Omega_{t=\tau_A} = 2$. The p values are: 0.50 (1), 1.00 (2), 1.20 (3), 1.25 (4)

Hence, from Fig. 2 we can deduce for $p = 1.25$ that τ_A exists for values $\chi_{t=\tau_A} < 20$, in agreement with Eq. (32).

Equation (17) can also be written in the form

$$J(\tau_A) = \frac{nF A_0 D^{1/2} C_A^*}{2aI_0}, \quad (33)$$

where

$$J(\tau_A) = \frac{\tau_A^{1/2}}{(t_1 + \tau_A)^{2/3}} [(1-p)S + pX]_{t=\tau_A}. \quad (34)$$

Thus, by means of linear regression of $J(\tau_A)$ vs $(nF A_0 D^{1/2} C_A^*)/(2I_0)$, it is possible to determine the anodic reaction order a of the anodic reaction from the value of the slope, according to Eq. (33).

Potential–Time Response

Figure 3 shows the dependence of $E-t$ curves on the rate constant k for a reversible process, when τ_A (Fig. 3a) and τ_B (Fig. 3b) are reached. This dependence is illustrated for a fixed value of $p = 0.5$, since these curves are affected by k for any p value. Note that τ_A increases with k (Fig. 3a), whereas τ_B decreases (Fig. 3b). its minimum value

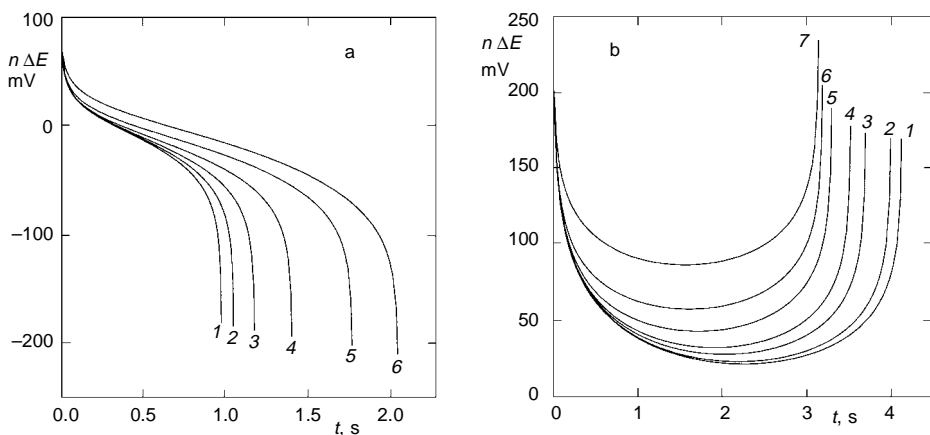


FIG. 3

The influence of k on the $E-t$ ($\Delta E = E(t) - E_c^0$) curves at an SMDE for a reversible charge transfer reaction. Parameters: $p = 0.5$, $\omega = 1 \text{ s}^{-1}$, $\xi_0 = 0.1 \text{ s}^{-1/2}$, $a = b = 1$ and $T = 298 \text{ K}$; for a: $N_{\text{SMDE}} = 3.2 \text{ s}^{-1/2}$, $k (\text{s}^{-1})$: $1 \cdot 10^{-2}$ (1), 1 (2), 3 (3), 10 (4), $1 \cdot 10^2$ (5), $1 \cdot 10^4$ (6); b: $N_{\text{SMDE}} = 0.7 \text{ s}^{-1/2}$, $k (\text{s}^{-1})$: $1 \cdot 10^{-2}$ (1), $1 \cdot 10^{-1}$ (2), $5 \cdot 10^{-1}$ (3), 1 (4), 3 (5), 10 (6), $1 \cdot 10^2$ (7)

corresponds to π/ω according to Eqs (18) and (A11) and it is independent of p (as follows from Eq. (18)).

In Fig. 4 we show the influence of concentration of electroactive species C_A^* for a reversible process when τ_B is reached and $N_{\text{DME}} t_s^{2/3}$ (Eq. (13)) remains constant. As can be deduced from Eq. (21), these curves are shifted to more positive potentials with growing C_A^* for $a > b$ (Fig. 4a) whereas the opposite effect is observed for $a < b$ (Fig. 4b). The $E-t$ curves are shown for a plane electrode, for $a = 2, b = 1, p = 0.5$ (refs^{17,18}) in Fig. 4a and for a plane electrode when $a = 1, b = 2$ and $p = 1.2$ (refs^{11,16}) in Fig. 4b.

The influence of k_c^0 is shown in Fig. 5 for $p = 1, k = 2 \text{ s}^{-1}, a = 2, b = 1, C_A^* = 1 \text{ mmol l}^{-1}, n = 2$ and $\alpha = 0.5$. From these curves and from Eqs (19), (20) and (24)–(27) it follows that the process becomes totally irreversible for $k_c^0 \leq 10^{-4} (\text{mmol l}^{-1})^{-1/2} \text{ cm s}^{-1}$. Under these conditions the potential–time response can be described by Eqs (24)–(27).

The influence of chemical kinetics is shown in Fig. 6 for irreversible charge transfer reaction and τ_B . The influence of k is similar to that found for a reversible process (Fig. 3b) with the exception of a shoulder⁸ disappearing at high values of k (curve 6).

The effects exerted by the electrode curvature for both SMDE and DME are more appreciable when species A is depleted at the electrode surface. These effects are less pronounced when oxidation transition time τ_B is observed instead.

In this technique the double layer effect is less markable at low frequencies and at higher concentrations of electroactive species. For this reason the frequencies of the alternating current considered in this paper are not higher than 2 Hz. Moreover, it is

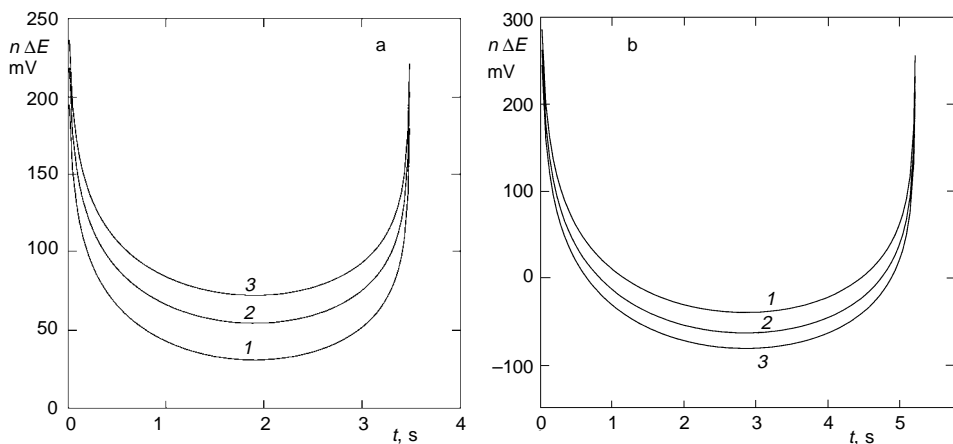


FIG. 4

The influence of C_A^* on the $E-t$ curves at a plane electrode for a reversible charge transfer reaction. Parameters: $k = 10^{-2} \text{ s}^{-1}, T = 298 \text{ K}, C_A^*$ (mmol l^{-1}): 1.0 (1), 2.5 (2), 5.0 (3). Conditions for a: $p = 0.5, \omega = 1.2 \text{ s}^{-1}, N_{\text{SMDE}} = 0.5 \text{ s}^{-1/2}, a = 2, b = 1$; for b: $p = 1.2, \omega = 0.8 \text{ s}^{-1}, N_{\text{SMDE}} = 1.5 \text{ s}^{-1/2}, a = 1, b = 2$

interesting to point out that these effects are lower when the electrode sphericity increases, *i.e.*, as the electrode radius becomes smaller.

Finally, it is also possible to determine the electrochemical kinetic parameters α and k_c^0 from Eqs (24)–(27) by means of linear regression of $E(t)$ vs $\ln g_C$ and/or $E(t)$ vs $\ln g_A$ plots, although in the latter case the order b must be known beforehand.

CONCLUSIONS

As shown above, the application of a sinusoidal current provides interesting informations for the study of regeneration mechanisms. It allows us to work always under conditions where the reduction (τ_A) or oxidation (τ_B) transition time is reached, in contrast to other electrochemical techniques. Although both transition times can be used for determining the rate constant of the chemical step, it seems more convenient to use the oxidation transition time τ_B since it is independent of the regeneration fraction values besides most experimental parameters, such as alternating current amplitude I_0 . Moreover, once the homogeneous kinetic constant is known, it is possible to determine the regeneration fraction and the anodic reaction order from the reduction transition time. In this way the use of sinusoidal current, which provides the information about τ_B (besides τ_A), seems appropriate for the study of regeneration processes and for distinguishing them from other mechanisms.

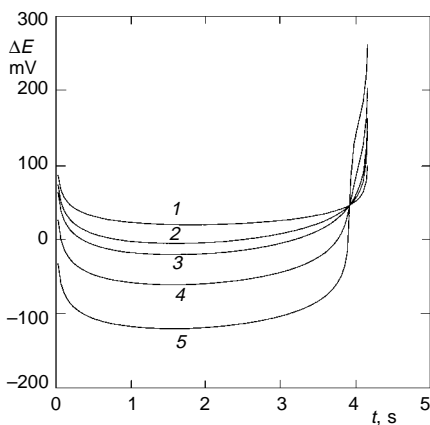


FIG. 5

Electrochemical reversibility effects on the $E-t$ curves at a DME for a total regeneration of species A (*i.e.* $p = 1$); $\omega = 0.8 \text{ s}^{-1}$, $t_1 = 1 \text{ s}$, $N_{\text{DME}}^{2/3} = 1.4 \text{ s}^{1/6}$, $D = 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, $\xi_0 = 0.1 \text{ s}^{-1/6}$, $a = 2$, $b = 1$, $n = 2$, $\alpha = 0.5$, $k = 2 \text{ s}^{-1}$, $C_A^* = 1 \text{ mmol l}^{-1}$, $T = 298 \text{ K}$. The values of k_c^0 in $(\text{mmol l}^{-1})^{-1/2} \text{ cm s}^{-1}$ are: 10^{-1} (1), 10^{-3} (2), $5 \cdot 10^{-4}$ (3), 10^{-4} (4), 10^{-5} (5)

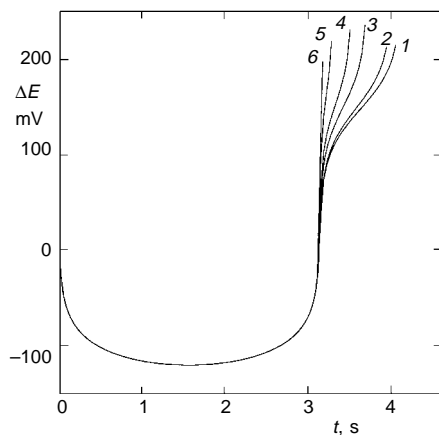


FIG. 6

Chemical rate constant effects on the $E-t$ curves at an SMDE for a totally irreversible charge transfer step when $p = 0.5$, $\omega = 1 \text{ s}^{-1}$, $N_{\text{SMDE}} = 0.7 \text{ s}^{-1/2}$, $D = 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, $\xi_0 = 0.1 \text{ s}^{-1/2}$, $a = b = 1$, $\alpha = 0.5$, $n = 2$, $k_c^0 = 10^{-5} \text{ cm s}^{-1}$ and $T = 298 \text{ K}$. The values of k (s^{-1}): 10^{-2} (1), 10^{-1} (2), $5 \cdot 10^{-1}$ (3), 1 (4), 3 (5), 10 (6)

The influence of the homogeneous rate constant on reduction and oxidation transition times is different. Thus, τ_A increases with k , whereas τ_B decreases to its minimum value $\tau_B = \pi/\omega$.

APPENDIX

The S and X series for a DME, obtained for the expanding sphere electrode, are defined as

$$S = S(\xi, \beta, \Omega) = \sum_{n=0}^{\infty} \frac{(-1)^n \Omega^{2n+1}}{(2n+1)!} J_{0,n}(\xi, \beta) \quad (A1)$$

$$X = X(\xi, \beta, \chi, \Omega) = \exp(-\chi) \sum_{j,n}^{\infty} \frac{(-1)^n \Omega^{2n+1}}{(2n+1)! j!} \chi^j J_{j,n}(\xi, \beta), \quad (A2)$$

where $J_{0,n}(\xi, \beta)$ may be considered as a particular case of $J_{j,n}(\xi, \beta)$, for $j = 0$, whose general expression is given by

$$J_{j,n}(\xi, \beta) = J_{j,n}^{(0)}(\beta) - \xi J_{j,n}^{(1)}(\beta) + \xi^2 J_{j,n}^{(2)}(\beta) \quad (A3)$$

$$J_{j,n}^{(0)}(\beta) = \frac{1}{p_{2j+4n+3}} \left\{ 1 + \frac{\beta^3}{3(2j+4n+5)} + \frac{7}{18} \frac{\beta^6}{(2j+4n+5)(2j+4n+7)} + \right. \\ \left. + \frac{20}{27} \frac{\beta^9}{(2j+4n+5)(2j+4n+7)(2j+4n+9)} + \dots \right\} \quad (A4)$$

$$J_{j,n}^{(1)}(\beta) = \frac{1}{4(j+2n+2)} + \frac{\beta^3}{8(j+2n+2)(j+2n+3)} + \\ + \frac{3}{32} \frac{\beta^6}{(j+2n+2)(j+2n+3)(j+2n+4)} + \dots \quad (A5)$$

$$J_{j,n}^{(2)}(\beta) = \frac{1}{p_{2j+4n+3}} \left\{ \frac{1}{2(2j+4n+5)} + \frac{\beta^3}{(2j+4n+5)(2j+4n+7)} + \dots \right\} \quad (A6)$$

Ω , χ , ξ and β are dimensionless parameters defined by relations

$$\Omega = \omega t \quad (A7)$$

$$\chi = kt \quad (A8)$$

$$\xi = \frac{2(Dt)^{1/2}}{r_0} \quad (A9)$$

$$\beta = \frac{t}{t_1 + t} = \frac{\Omega}{\Omega_1 + \Omega} ; \quad \Omega_1 = \omega t_1 . \quad (A10)$$

When the blank period t_1 does not exist ($t_1 = 0$) the response can be deduced from Eqs (11) and (12) by setting $\beta = 1$ in Eqs (A1)–(A6).

The X series has an asymptotic solution, which may be obtained when the steady-state approximation is applied. Thus, for large values of χ , the X series is simplified to the following expression

$$X = \frac{\sin(\omega t)}{2\chi^{1/2}} \quad (\chi \geq 20) \quad (A11)$$

which remains valid for any type of electrode such as DME, SMDE and stationary plane electrode.

Conversely, for small values of the argument the following limit is obtained

$$\lim_{\chi \rightarrow 0} X = S . \quad (A12)$$

As indicated above, the S and X series have been deduced for a DME adopting the expanding sphere electrode model. Nevertheless, they allow us to deduce relations corresponding to a static spherical electrode (SMDE) and a planar electrode (PE) by the following procedure:

Static Spherical Electrode

The response for a static electrode of area $A = A_0 t_1^{2/3}$ can be found assuming $t_1 \gg t$ (or $\beta = 0$) in Eqs (A1)–(A6) and by substituting N_{DME} for N_{SMDE} in Eqs (11), (12) and (19)–(27), where

$$N_{\text{SMDE}} = \frac{2I_0}{nFAD^{1/2}C_A^*} \quad (A13)$$

The S and X series for an SMDE are then simplified to

$$S_{\text{SMDE}} = \sum_{n=0}^{\infty} \frac{(-1)^n \Omega^{2n+1}}{(2n+1)!} \left[\frac{1}{p_{4n+3}} - \frac{1}{4(2n+2)} \xi + \frac{1}{2p_{4n+3}(4n+5)} \xi^2 + \dots \right] \quad (A14)$$

$$X_{\text{SMDE}} = \exp(-\chi) \sum_{j,n}^{\infty} \frac{(-1)^n \Omega^{2n+1}}{(2n+1)! j!} \chi^j \left[\frac{1}{p_{2j+4n+3}} - \frac{1}{4(j+2n+2)} \xi + \right. \\ \left. + \frac{1}{2p_{2j+4n+3}(2j+4n+5)} \xi^2 + \dots \right] \quad (A15)$$

Regarding the transition times of oxidized and reduced species, Eq. (17) for this electrode is simplified to

$$\tau_A^{1/2} = \frac{nFAD^{1/2}C_A^*}{2aI_0[(1-p)S + pX]_{t=\tau_A}} \quad (A16)$$

whereas Eq. (18), corresponding to τ_B , remains valid.

The condition $C_A(r_0, \tau_A) = 0$ is valid when N_{SMDE} is higher than a fixed minimum value given by

$$N_{\text{min}} = \left(\frac{2I_0}{nFAD^{1/2}C_A^*} \right)_{\text{min}} = \frac{1}{aH_{\text{max}}} \quad (A17)$$

see Eqs (11) and (A13), where H_{max} is the absolute maximum of the H function vs time defined as

$$H = [(1-p)S + pX] t^{1/2} \quad (A18)$$

Finally, Y in Eq. (30) is then given by

$$Y = \frac{(S)_{t=\tau_A}}{(S)_{t=\tau_A^c}} \quad (A19)$$

and Eq. (A16) may also be written in the form

$$J(\tau_A) = \frac{nF AD^{1/2} C_A^{*}}{2aI_0}, \quad (A20)$$

where

$$J(\tau_A) = \tau_A^{1/2} [(1-p)S + pX]_{r=\tau_A}. \quad (A21)$$

Plane Electrode

The response for this static electrode of area $A = A_0 t_s^{2/3}$ may be obtained from that deduced above for an SMDE by setting $\xi = 0$ in Eqs (A14) and (A15).

LIST OF SYMBOLS

a, b	cathodic and anodic reaction orders
$A(t_s)$	time-dependent area for a DME ($A = A_0 t_s^{2/3}$)
A_0	electrode area for $t_s = 1$ s ($A_0 = (4\pi)^{1/3} (3m_{\text{Hg}}/d)^{2/3}$)
C_A	concentration of species A
C_B	concentration of species B
E_c^0	formal potential of the electrode reaction (in concentration scale)
$E(t)$	time-dependent electrode potential
k	rate constant corresponding to the chemical step
$k_{\text{red}}, k_{\text{ox}}$	electrode reaction rate constants for the reducing (cathodic) and the oxidizing (anodic) reactions, respectively
k_c^0	conditional rate constant of an electrode reaction
m_{Hg}, d	rate of flow and density of mercury
n	number of electrons transferred in the charge transfer step
p	regeneration fraction
p_j	$2\Gamma(1+j/2)/\Gamma((1+j)/2)$
r	distance from the center of the electrode
r_0	electrode radius at time t_s for a DME ($r_0 = \zeta t_s^{1/3}$) or fixed electrode radius for an SMDE
t	time elapsed between the application of the alternating current and the potential measurement
t_1	blank period used, optionally, only with non-stationary electrodes (DME)
t_s	$= t_1 + t$
α, α'	cathodic and anodic transfer coefficients
β	$= t/(t_1 + t) = \Omega/(\Omega_1 + \Omega)$
Γ	Euler gamma function
ζ	radius of DME for $t_s = 1$ s ($= (3m_{\text{Hg}}/4\pi d)^{1/3}$)
ν	stoichiometric number for the electrode reaction
ξ	dimensionless parameter ($\xi = 2(Dt)^{1/2}/r_0$)

ξ_0	= $\xi/t^{1/2}$ for an SMDE and $\xi t_s^{1/3}/t^{1/2}$ for a DME
τ_A	reduction transition time of species A
τ_B	oxidation transition time of species B
τ_A^s	reduction transition time of species A for an E mechanism
τ_B^s	oxidation transition time of species B for an E mechanism
χ	= kt
ω	angular frequency of alternating current ($2\pi f$ where f is the conventional frequency in Hz)
Ω	= ωt
Ω_1	= ωt_1

Other symbols have conventional meaning.

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