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APPLICATION OF CONTROLLED-POTENTIAL COULOMETRY TO REACTION KINETICS OF SPECIES AT TRACER SCALE CONCENTRATION : «THE RADIOCOULOMETRY».

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ABSTRACT.

The theoretical treatment of controlled-potential coulometric method in the presence of kinetic effects has been investigated in the case of amalgamation electrode reactions. It showed that kinetic studies of these reactions can be undertaken by this technique even for elements at tracer scale concentrations (Radiocoulometry) using radioactive tracer.

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Introduction.

The current-potential curves obtained with any classical electrochemical method require the presence of the studied electroactive species in the bulk of the electrolyte at concentrations higher than 10^{-6}M. In order to pass through this limit ($\sim 10^{-9}$M) it is necessary to investigate special techniques and sophisticated equipment ; however, it is a fact that whatever the performance of the method is, the current seems to be unmeasurable for extremely diluted electrolytes (i.e. concentrations less than 10^{-10}M). That is the case for transplutonium elements ($95 \leq Z \leq 103$) which are usually available at tracer scale (from 10^{-8}M to 10^{-16}M). To get over the current measurement when such elements are investigated in electrochemical methods, we applied radiochemical determinations using radioisotopes that lead to measure the radioactivity and hence the concentration of the oxidised or reduced substance. Under these conditions, the only electrochemical reactions that could be studied are those leading to the formation of the oxidised and reduced substances onto two different phases : the electrolyte and the electrode. This is typically the case of amalgamation reactions. The radioactivity of elements collected in the mercury is proportional to its amount and hence proportional to the corresponding current. This principle was simply applied to adapt polarographic methods (1) and to devise the "Radiopolarography" which is now successfully used to determine half-wave potentials of reactions of type :

$$M^{n+} + ne + Hg \rightleftarrows M(Hg)$$

for some transplutonium elements at tracer scale (2).

In this work, we devised similarly the "Radiocoulometry" as a practical method to study electrochemical behavior of cations at tracer scale.

The method of coulometry is often used to determine the number n of electrons involved in the overall studied reactions. In most cases the current-time curve is obtained. In some other cases, the variations of the concentration C of the electroactive species with electrolysis time t, is observed by coupling a polarograph to the coulometric circuit, and the slope of the linear curve log $C = f(t)$ should give n (3). In both cases, the controlled potential is adjusted at values where kinetic effects are avoided, i.e. the potential of the working electrode is chosen in the potential range of diffusion limiting current of the corresponding current-potential curve. Under this condition the rate constant of diffusion process has been measured for electrochemical amalgamation reactions with species at tracer scale concentration (4).

In the following, we consider the general case of electrolysis at constant potential taking into account the kinetic effect of the electrochemical reaction on the shape of concentration-time curves and hence on the shape of current-time curves. The corresponding expressions obtained in the case of amalgamation reaction are similar to those reported by A.Bard and K.Santhanam (5) in the case of quasi reversible electrode process.

The final purpose is to adapt these equations to radiochemical investigations using radioactive elements at tracer scale concentration.

Theoretical treatment.

The only significant criterion that could replace the current measurement in case of coulometry with extremely diluted electroactive species, is its concentration C in the bulk of electrolyte which varies with time of electrolysis, for electrode process involving a forming amalgam metal. The derivation of the equation $C = f(t)$ should express a quantitative relation between the variation of C and the rate of the electrode process.

We consider in this treatment the electrode process with amalgam formation and assume that the electrochemical reaction involves a single rate determining step so that it can be written in the form :

$$M^{n+} + ne + Hg \underset{k_e^+}{\overset{k_e^-}{\rightleftarrows}} M(Hg)$$

The number of moles of M^{n+} being consumed per unit of time and per unit of area is

$$\frac{dN}{dt} = k_e^- C_e - k_e^+ C_a \tag{1}$$

where C_e and C_a are respectively the concentration of M^{n+} in the electrolyte and of M in mercury. k_e^- and k_e^+ are the rate constants for the forward and backward electrode process respectively. These constants can be expressed in terms of standard constant rate k_e° and standard electrode potential E° of the couple $M^{n+}/M(Hg)$ with the well-known following expressions :

$$k_e^- = k_e^\circ \exp\frac{-\alpha nF}{RT}(E-E^\circ) \tag{2a}$$

$$k_e^+ = k_e^\circ \exp\frac{(1-\alpha)nF}{RT}(E-E^\circ) \tag{2b}$$

Further we assume that mass transfer in the bulk of electrolyte is ensured by stirring, and under the influence of diffusion at the electrode surface. Therefore, the rate given in equation (1) can be expressed according to the first Fick's law :

$$-\frac{dN}{dt} = D_1 \left(\frac{\partial C}{\partial x}\right)_{x=0} \tag{3a}$$

If a steady state existing at the interface is assumed, this rate can be also expressed in terms of concentration gradient of M in the mercury :

$$\frac{dN}{dt} = D_2 \left(\frac{\partial C_{Hg}}{\partial x}\right)_{x=0} \tag{3b}$$

D_1 and D_2 denote the diffusion coefficients of M^{n+} in the electrolyte and the mercury respectively. In other words, the sum of fluxes for M^{n+} and M at the electrode surface is equal to zero :

$$D_1\left(\frac{\partial C}{\partial x}\right)_{x=0} + D_2\left(\frac{\partial C_{Hg}}{\partial x}\right)_{x=0} \tag{4a}$$

According to Nernst concept of diffusion layer (see figure (1)), equation (4a) can be written in the form :

$$D_1\left(\frac{C-C_e}{\delta_1}\right) + D_2\left(\frac{C_{Hg}-C_a}{\delta_2}\right) = 0 \tag{4b}$$

In addition, the number of moles of M^{n+} consumed $-(\frac{dN}{dt})$ at the electrode surface involves a corresponding decrease of concentration $-\frac{dC}{dt}$ on the bulk of electrolyte so that :

$$\frac{dC}{dt} = \frac{S}{V_1}\frac{dN}{dt} \qquad (5)$$

where S is the area of mercury electrode and V_1 the volume of electrolyte. Finally, as initial condition, we assume that at time t=0 the concentration C_{Hg} of M in the mercury of volume V_2 is equal to zero, and the concentration of M^{n+} in the electrolyte is C°. This leads to the following equation that expresses the "balance" of the reaction at any instant t of electrolysis :

$$V_1(C^\circ - C) = V_2\, C_{Hg} \qquad (6)$$

Expressing the flux $\frac{dN}{dt}$ in terms of $\frac{dC}{dt}$ from equation (5) and combining equations (4b) and (6) with equation (1) lead to the following differential equation :

$$\left(\frac{D_2\delta_1}{\delta_2 D_1} + \frac{k_e^+}{k_e^-} + \frac{D_2}{\delta_2 k_e^-}\right)\frac{dC}{dt} + \frac{S}{V_1}\frac{D_1}{\delta_1}\left(1 + \frac{V_1}{V_2}\frac{k_e^+}{k_e^-}\right)C = \frac{S\, D_1\, V_1\, k_e^+\, C^\circ}{V_1\,\delta_1\, V_2\, k_e^-} \qquad (7)$$

In order to simplify the presentation of the general integration of this equation, we regrouped the different parameters under the following abridged forms :

$$A = \frac{D_2\delta_1}{\delta_2 D_1}\ ,\ a_1 = \frac{D_1}{\delta_1}\ ,\ f = \frac{S}{V_1}\frac{D_1}{\delta_1}\ ,\ b = \frac{V_1}{V_2}$$

$$K = \frac{k_e^+}{k_e^-} = \exp\frac{nF}{RT}(E-E^\circ) \quad \text{and} \quad k_e^- = K^{-\alpha}$$

Thus, the general integration of equation (7) can be written :

$$\frac{C}{C^\circ} = \left(1 - \frac{bK}{1+bK}\right)\exp\left[-fA\left(\frac{1 + bK}{A+K+\frac{a_2}{k_e^\circ}K^\alpha}\right)\right]t + \frac{bK}{1+bK} \qquad (8)$$

which exhibits an exponential decrease of the concentration C with time of electrolysis. This variation of C is essentially E, k_e° and α dependent. In addition, when the time of electrolysis is sufficiently long, the concentration C should attain a limit which is derived from equation (8) by neglecting the first term of the second member, so that :

$$\left(\frac{C}{C^\circ}\right)_{t\to\infty} = \frac{bK}{1+bK} \qquad (9)$$

This equation can be written in the following form :

$$E = E^\circ - \frac{2.3RT}{nF}\ \log\frac{V_1}{V_2} - \frac{2.3RT}{nF}\ \log\frac{C^\circ - C_{t\to\infty}}{C_{t\to\infty}} \qquad (10)$$

which is similar to the Nernst equation caracterizing reversible equilibrium.

The effect of the mentionned parameters (E, E°, k°_e and α) can be illustrated from the calculated curves $C = f(t)$ plotted in figure (2) for different values of $(E-E^\circ)$, k°_e and α being constant. On the other hand the curves $C = f(t)$ in figure (3) show the effect of the standard rate constant k°_e on the shape of the curves plotted at a constant potential. A qualitative examination of these latter curves shows that the limit $\left(\frac{C}{C^\circ}\right)_{t\to\infty}$ is more or less rapidly attained according to the rate constant k°_e ; e.g. for reversible electrode processes ($k^\circ_e > 10^{-3}\,\mathrm{cm.s^{-1}}$), the limit $\left(\frac{C}{C^\circ}\right)_{t\to\infty}$ should be observed after 5 to 20 minutes of electrolysis, whereas this same limit is obtained after more than 120 minutes for irreversible electrode process ($k^\circ_e < 10^{-5}\,\mathrm{cm.s^{-1}}$). This property can be quantitatively examined by considering the exponential term related to the time t. For this, it is useful to derive from equation (8) the expression of the time τ of half-reaction (usually called period), defined as the time needed to consume the half of moles of M^{n+} present at $t = 0$:

$$\left(\frac{C}{C^\circ}\right)_{t=\tau} = \frac{1}{2}\ .$$

On the other hand, τ can be expressed in terms of the slope-G° of the tangent at the origin to the curve $C = f(t)$ or $\log C = f(t)$

$$\tau = \frac{0.693}{G^\circ} \qquad (11)$$

with :

$$G^\circ = -\left[\frac{d\left(\frac{C}{C^\circ}\right)}{dt}\right]_{t=0} = -\left[\frac{d\left(\log\frac{C}{C^\circ}\right)}{dt}\right]_{t=0} \qquad (12)$$

or

$$G^\circ = \frac{fA}{A + K + \frac{a_2}{k^\circ_e}K^\alpha} \qquad (13)$$

Therefore :
$$\tau = \frac{0.693(A + K + \frac{a_2}{k_e^\circ} K^\alpha)}{fA} \qquad (14)$$

Replacing now the abridged functions f, A, K and a_2 by their values one obtains the following equation for the half-reaction time τ :

$$\tau = 0.693 \frac{V_1\delta_1}{S\,D_1} \left[1 + \frac{D_1\delta_2}{\delta_1 D_2} \exp\frac{nF}{RT}(E-E^\circ) + \frac{D_1}{\delta_1 k_e^\circ} \exp\frac{\alpha nF}{RT}(E-E^\circ)\right] \qquad (15)$$

which includes three terms. As we will see next, according to the imposed value E and to the value of k_e° one or two of these terms can be neglected and τ takes simpler forms.

a. Reversible electrode process.

In this case equation (15) takes the following form, by neglecting the third term

$$\tau(I) = 0.693 \frac{V_1\delta_1}{S\,D_1} \left[1 + \frac{\delta_2 D_1}{D_2\delta_1} \exp\frac{nF}{RT}(E-E^\circ)\right]$$

This equation exhibits an exponential decrease of $\log\tau(I)$ with the cathodic potential E. The figure (4) (curve b) shows a theoretical curve $\log\tau(I) = f(E-E^\circ)$ in which a linear variation with a slope of $\frac{nF}{2.3RT}$ is stated at sufficiently positive values of $(E-E^\circ)$. When $E-E^\circ$ is sufficiently negative the curve tends toward a limiting constant value $\tau(III)$:

$$[\tau(I)]_{E<<E^\circ} \rightarrow \tau(III)$$

with

$$\tau(III) = 0.693 \frac{V_1\delta_1}{S\,D_1} \qquad (17)$$

b. Irreversible electrode process.

The equation of the period τ defined in this case as $\tau(II)$ is derived from equation (15) by neglecting the second term :

$$\tau(II) = 0.693 \frac{V_1\delta_1}{S\,D_1} \left[1 + \frac{D_1}{\delta_1 k_e^\circ} \exp\frac{\alpha nF}{RT}(E-E^\circ)\right] \qquad (18)$$

The theoretical curve $\log\tau(II) = f(E-E^\circ)$ plotted in figure (4)(curve a) exhibits a similar shape for $\log\tau(I) = f(E-E^\circ)$ but the slope is equal to

$\frac{\alpha nF}{2.3RT}$ instead of $\frac{nF}{2.3RT}$; the curve attains the same limiting value $\tau(III)$:

$$[\tau(II)]_{E<<E^\circ} \rightarrow \tau(III)$$

It is of interest to keep in mind the particular value E_2 which corresponds to the intersection of $\tau(II)$ and $\tau(III)$. The value of E_2 is easily obtained by equating $\tau(II) = f(E-E^\circ)$ (eq.18) with $\tau(III)$(eq.17) :

$$E_2 = E^\circ - \frac{2.3RT}{\alpha nF} \log \frac{D_1}{\delta_1 k_e^\circ} \qquad (19)$$

This relation shows that E_2 represents the half-wave potential obtained from current-potential curve for irreversible electrode process. This property emphasizes the fact that the experimental curve $\log\tau = f(E)$ leading to the determination of E_2 could be an accessible method to study kinetics of electrode processes.

In order to understand the fact that half-time reaction τ could be a useful parameter which replace the corresponding current i, it is of interest to show the simple relationship between τ and i. We aim for that to find the parallelism between equation $\tau = f(E)$ and $i = f(E)$. The current i° exchanged at the beginning of the electrolyse (t=0), is proportional to the corresponding flux $(\frac{dN}{dt})_{t=0}$. Thus :

$$i^\circ = (\frac{dN}{dt})_{t=0}\, nFS \qquad (20)$$

On the other hand according to equation (13) :

$$\tau = \frac{0.693}{G^\circ} \qquad (13)$$

in which G° denotes the absolute value of the slope of the tangent at the origin of $C = f(t)$

$$G^\circ = -\left[\frac{d(\frac{C}{C^\circ})}{dt}\right]_{t=0} \qquad (11)$$

or

$$G^\circ = (\frac{dN}{dt})_{t=0} \frac{S}{V_1 C^\circ} \qquad (21)$$

one can easily relate i° to τ by combining equations (20), (13) and (21) :

$$i^\circ = \frac{0.693\ nF\ V_1 C^\circ}{\tau} \qquad (22)$$

in such a way similarly one can relate the limiting current i_d° to the corresponding period $\tau(III)$

$$i_d^\circ = \frac{0.693\ nF\ V_1\ C^\circ}{\tau(III)} \qquad (23)$$

or

$$i_d^\circ = nFS\,\frac{D_1}{\delta_1}\,C^\circ \qquad (24)$$

Replacing in the general equation (15), τ and the term $\frac{D_1}{\delta_1}$ by their values in terms of i° and i_d° from equations (22) and (24) respectively, one obtains the general equation of current-potential curves :

$$\frac{i^\circ}{i_d^\circ} = \frac{1}{1 + \frac{D_1\delta_2}{\delta_1 D_2}\exp\frac{nF}{RT}(E-E^\circ) + \frac{D_1}{\delta_1 k_e^\circ}\exp\frac{\alpha nF}{RT}(E-E^\circ)} \qquad (25)$$

Therefore the functions $\tau = f(E)$ and $i^\circ = f(E)$ include the same parameters of the electrode process. In addition, since τ is related to the reversal corresponding current : $\tau = f(\frac{1}{i^\circ})$, the homologous form of the well-known $\log\frac{i^\circ}{i_d^\circ - i^\circ} = f(E)$ equation is $\log\frac{\tau(III)}{\tau - \tau(III)} = f(E)$ (fig.5).

Radiocoulometry.

The above treatment showed that for electrochemical reactions involving a forming amalgam metal the time τ of half-reaction is a suitable parameter to study the oxidation-reduction behavior of species at the mercury cathode. It permits to get out of measuring the current, and therefore ables one to investigate elements at tracer scale concentrations. In this latter case radioisotopes are used and concentrations are measured with a good precision by following the radioactivity of the solution during the electrolysis. Accordingly we propose to call this method "radiocoulometry". It permits exclusively to study simultaneously several electroactive species even electrochemically similar, in the same mixture provided that they can be radiochemically selected. This selection is based on the nature or the energy of their rays emitted. In an ulterior article this treatment will be applied to interpret experimental data on some transplutonium elements.

References.

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Figure captions.

Figure 1. Variations of the concentration C and C_{Hg} of the reacting species with distance from the electrode in both phases of volume V_1 and V_2. δ_1 and δ_2 are the thicknesses of the diffusion layers in the electrolyte and the mercury respectively, C_e and C_a the concentrations of M^{n+} and M at the electrode.

Figure 2. Variations of $\log\frac{C}{C°}$ with time of electrolysis for different values of E-E°. The curves are plotted from equation (8) with $\frac{S}{V_1} = 1$, $\frac{V_1}{V_2} = 2$, $a_2 = a_1 = 9.10^{-4}$ and $k_e^\circ = 10^{-2} cm.s^{-1}$, $\alpha = 0.5$.

Figure 3. Variations of $\log\frac{C}{C°}$ with the time of electrolysis showing the effect of the standard constant rate k_e° on the shape of the curves. The value (E-E°) is maintained constant [E-E° = -10 mV], as well as the other parameters in equation (8) :
$a_2 = a_1 = 9.10^{-4}$, $\frac{S}{V_1} = 1$, $b = 2$, $\alpha = 0.7$
(c) $k_e^\circ = 10^{-5} cm.s^{-1}$
(b) $k_e^\circ = 5.10^{-5} cm.s^{-1}$
(a) $k_e^\circ = 10^{-2} cm.s^{-1}$.

Figure 4. Variations of the half-reaction time τ with the imposed potential (E-E°) (equation (1)).
(a) irreversible electrode process ($k_e^\circ = 5.10^{-6} cm.s^{-1}$ and $\alpha = 0.3$;
(b) reversible electrode process ($k_e^\circ = 10^{-2} cm.s^{-1}$).

Figure 5. The theoretical curves $\log\frac{\tau(III)}{\tau-\tau(III)}$ for reversible and irreversible electrode processes are parallel to the well-known curves $\log\frac{i°}{i_d^\circ - i°} = f(E-E°)$.

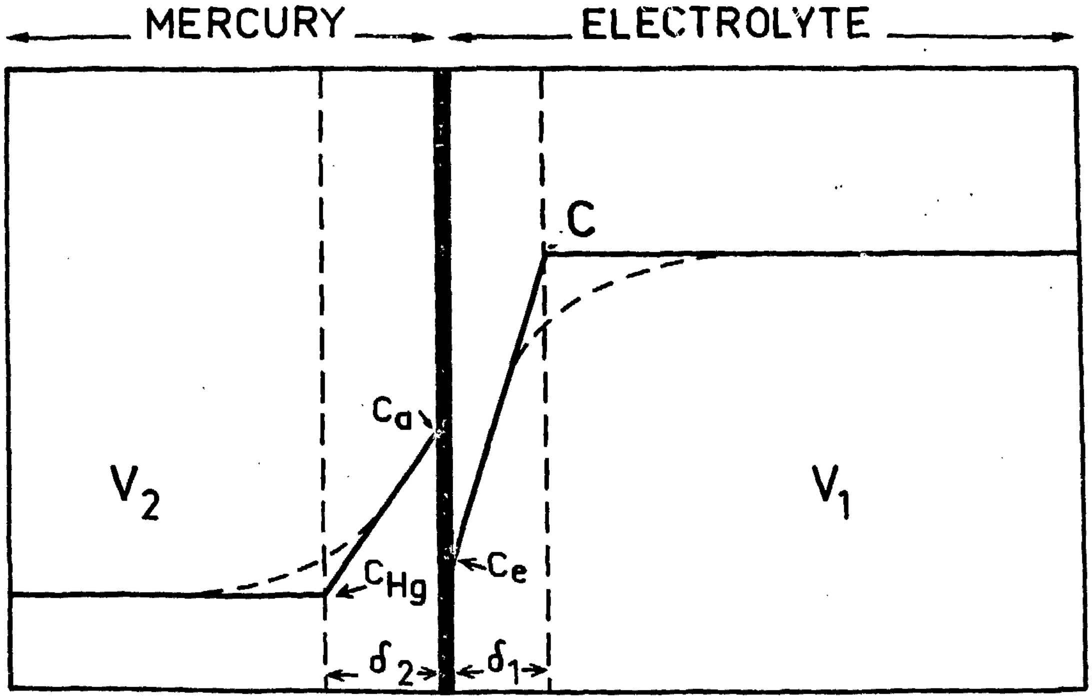


Fig. 1

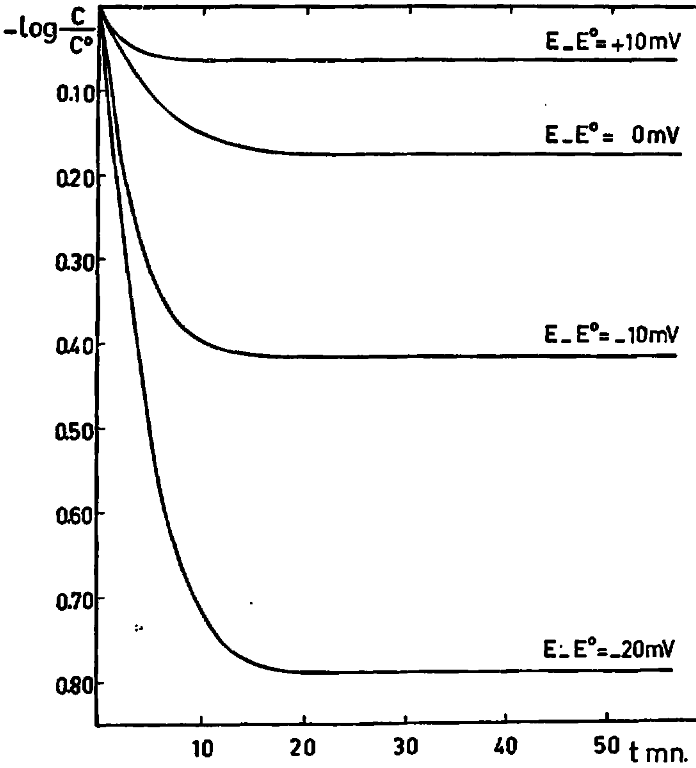

-log C/C°
0.10
0.20
0.30
0.40
0.50
0.60
0.70
0.80
E_E°=+10mV
E_E°= 0mV
E_E°=_10mV
E_E°=_20mV
10
20
30
40
50
t mn.

FiG 2

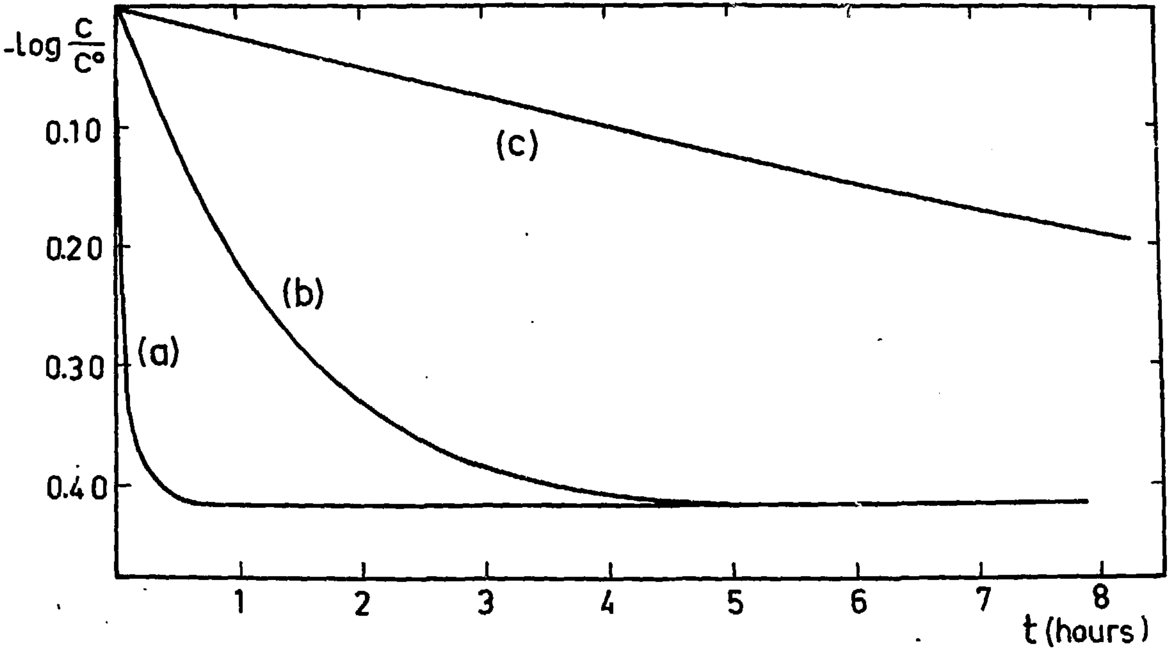
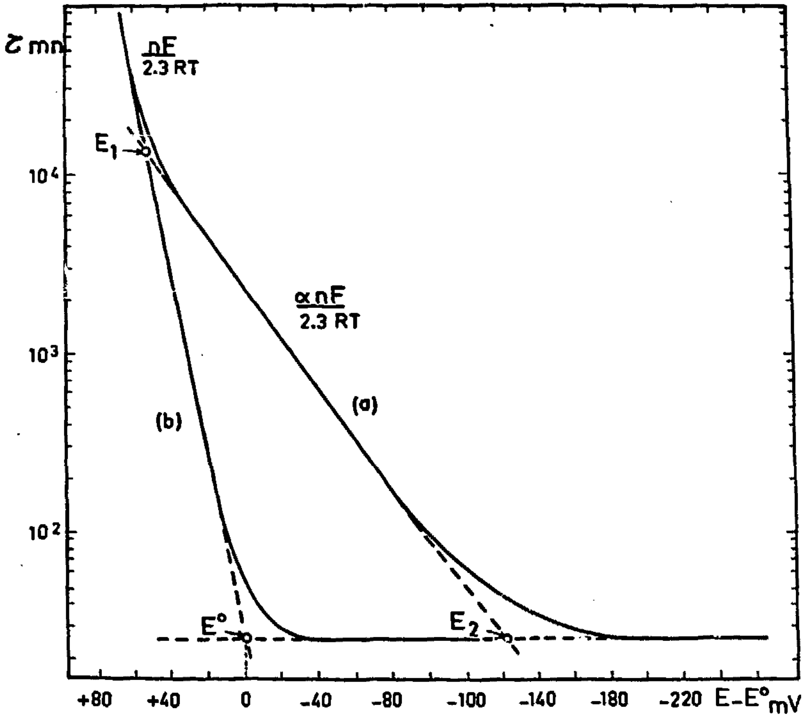


FIG. 3



τ mn
nF / 2.3 RT
E1
10^4
10^3
10^2
αnF / 2.3 RT
(a)
(b)
E°
E2
+80
+40
0
-40
-80
-100
-140
-180
-220
E–E° mV

Fig 4

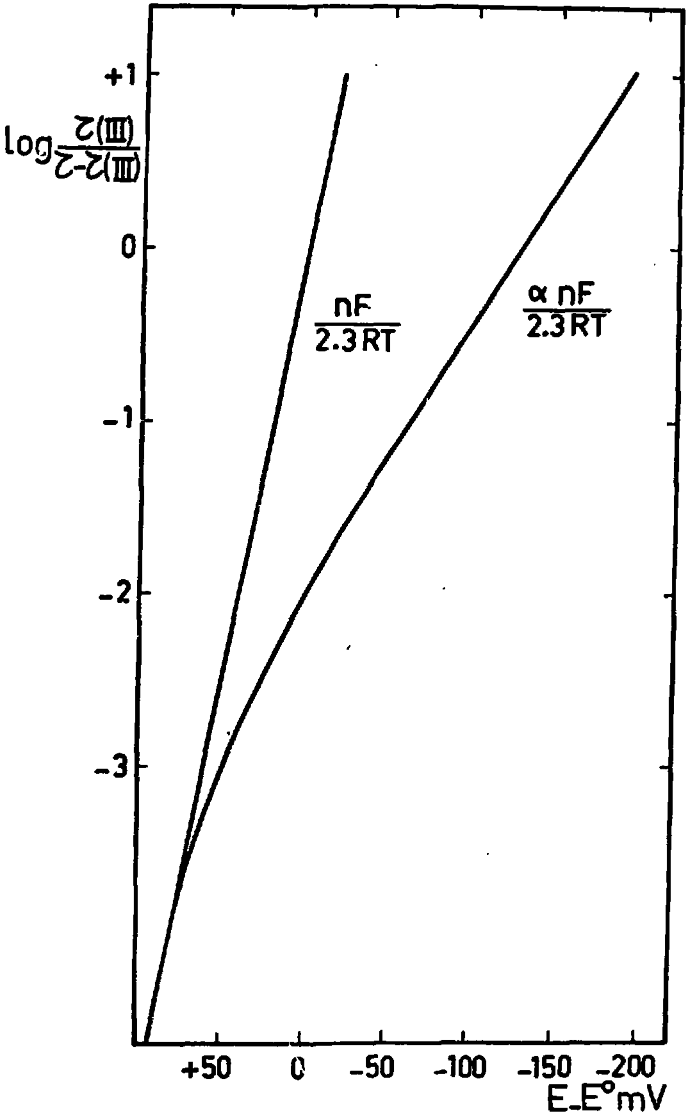

+1
log $\frac{\tau(III)}{\tau-\tau(III)}$
0
$\frac{nF}{2.3RT}$
$\frac{\alpha nF}{2.3RT}$
-1
-2
-3
+50
0
-50
-100
-150
-200
E-E°mV

Fig. 5