COMPARATIVE POSSIBILITIES OF INVERSE METHODS OF ELECTROCHEMICAL ANALYSIS

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Contemporary inverse methods of electrochemical analysis make use of concentration of material in the form of an amalgam [1, 2] or solid phase [2, 3]. Information on the composition of a solution is obtained mainly by the use of polarization curves for the dissolution of amalgams, metals, or chemical compounds, with an electrode potential which alters linearly with time. There are numerous statements in the literature as to the possibility of carrying out both [4] or one [5] of these states at a given current, but the latter is mainly used in amalgam variants [6].

The object of the present paper is to estimate the possibilities of using various electrode polarization conditions in analytical and partly electrochemical investigations. We have restricted our considerations of category of process to the ionization of metals at the surface of an indifferent solid electrode, uncomplicated by chemical stages [7, 8], and we make use of literature data and our own specially made calculations. It is assumed that the determination always consists of two stages. The first involves accumulation (deposition) of the metal under stationary hydrodynamic conditions. It is completed by de-excitation of the solution. The second stage, ionization of the metal, is carried out with a quiescent solution, which contains an adequate concentration of indifferent electrolyte. Electrolysis is carried out under conditions such that depletion of the solution can be neglected.

Let us consider the features which characterize the stage of accumulation and oxidation (deposition of metal), for various electrode polarization conditions.

The following symbols are used:

a and a_∞ are the activities of the deposit on the electrode and of the corresponding macrophase respectively [3];

$C(0, t)$ is the concentration of discharging ions close to the electrode;

C^0 is the concentration of ions in the bulk of the solution;

D is the diffusion coefficient;

F is the Faraday number;

i_d is the limiting diffusion current for the ion to be determined;

K_S is the rate constant for the electrode process at standard potential;

n is the number of electrons;

Q is the quantity of electricity equivalent to the amount of metal deposited;

S is the electrode area;

t is time;

t_r is the relaxation time;

v is the rate of change of potential;

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TABLE 1. Relations between Parameters for the Process of Electrodissolution of Metal at a Potential Varying Linearly with Time [3]. Recorded Relation $i = f(\varphi)$

Process	Reversible		Irreversible	
Equations relating main parameters	Microphase $I = -0,29\ \frac{nF}{RT} VQ$ $\varphi_t = \varphi_e + \frac{RT}{nF} \times \ln \frac{\tau_{de}}{\delta} \sqrt{\frac{nF}{RT} DV}$	Macrophase $I = -0,93\ \frac{nF}{RT} VQ' + 0,93 \frac{nF}{RT} VQ$	Microphase $I = 0,37 \frac{nF}{RT}\ \beta VQ$ $\varphi_m = \varphi^0 + \frac{TR}{\beta nF} \times \ln \frac{\beta V}{RTSK_S\gamma}$	Macrophase $I = -0,93 \frac{nF}{RT} \beta VQ' + 0,835\ \frac{nF}{RT} \beta VQ$
Parameters of process which can be determined	n, γ		βn, K_S, γ	
Values depending on concentration and the character of this relationship	The maximum anode current is proportional to the concentration for dissolution of the microphase, and varies linearly with concentration for dissolution of the macrophase			

α and β are the transport numbers for the electrode process;

γ is a proportionality coefficient;

δ is the thickness of the diffusion layer;

τ_{de} is the time taken for deposition;

τ_c is the conversion time;

φ is the electrode potential;

φ_e is the equilibrium potential;

φ^0 is the standard potential,

$$\varphi^0 = \varphi_1^0 - \frac{RT}{nF} \ln a_\infty .$$

Accumulation Stage

Given a Constant Electrode Potential. The quantity of metal, or the equivalent quantity of electricity Q, is determined by the relationship:

$$Q = nFSD \frac{C^0 - C(0, t)}{\delta} \tau_{de}. \quad (1)$$

At the potential corresponding to the limiting diffusion current of the ion $C(0, t) = 0$, so that

$$Q = nFSD \frac{C^0 \tau_{de}}{\delta}. \quad (2)$$

Equation (1) converts into the well known equation (2) and agrees well with experimental data [9], which shows a direct proportionality between concentration and quantity of metal deposited.

Given a Constant Current (i). A. $i < i_d$, then

$$i = nFSD \left.\frac{\partial C}{\partial x}\right|_{x=0} = \text{const}. \quad (3)$$

Under stationary hydrodynamic conditions (δ = constant) (stirred solution):

$$i = nFSD \frac{C^0 - C(0,t)}{\delta}. \quad (4)$$

TABLE 2. Relations between Parameters for the Process of Electrodissolution of the Metal at a Constant Current [5, 13]. Recorded Relation $\varphi = f(t)$

Process	Reversible		Irreversible	
Equations relating main parameters	Microphase $\varphi=\varphi^\circ+\frac{RT}{nF}\ln\frac{1}{\gamma}\times\left(C^\circ+\frac{2i}{nFS}\sqrt{\frac{t}{\pi D}}\right)-\frac{RT}{nF}\ln(Q-it)$ $\tau_c=Q/i$	Macrophase $\varphi=\varphi^\circ+\frac{RT}{nF}\times\ln\left(C^\circ+\frac{2i}{nFS}\times\sqrt{\frac{t}{\pi D}}\right)$ $\tau_c=Q/i$	Microphase $\varphi=\varphi^\circ+\frac{RT}{\beta nF}\times\ln\frac{i}{nFSK_S\gamma}-\frac{RT}{\beta nF}\ln(Q-it)$ $\tau_c=Q/i$	Macrophase $\varphi=\varphi^\circ+\frac{RT}{\beta nF}\times\ln\frac{i}{nFSK_S}$ $\tau_c=Q/i$
Parameters of process which can be determined	n, γ		β_n, K_S, γ	
Values depending on concentration and the character of this relationship	The conversion time of the process is directly proportional to the concentration			

Equation (1) should apply to the relationship between the quantity of metal deposited in the accumulation process and the concentration of its ions in the solution.

B. $i > i_d$. In this case the quantity of metal ions discharging at the electrode is determined by the limiting diffusion current of the ion, and should conform with equation (2).

Thus, direct proportionality between the quantity of metal deposited and the concentration of the corresponding ion in solution can be obtained only at a constant potential, corresponding to the limiting diffusion current, or at a constant current exceeding the limiting diffusion current for the discharging ion. However, in the latter case, the process of discharge of the ions to be determined is not a single electrode process. Any more electronegative element will be discharged at the electrode at the same time. The quantity of it, at any given current, will be greater the lower the concentration of the ion to be determined. Oxidation of the foreign material deposited can make it difficult to measure the latter.

We will assume below that the accumulation stage is carried out under conditions such that equation (2) applies, i.e., the quantity of metal deposited on the electrode is proportional to the concentration of its ions in solution.

Dissolution Stage

Given a Potential Varying Linearly with Time (Inverse Voltamperometry [3]). The principal measured value, under these conditions of electrode polarization is the maximum current for electrodissolution of the metal (Table 1). Between this value and the amount of metal deposited in the accumulation stage, there is a proportional relationship for dissolution of a microphase, or a linear relationship for dissolution of a macrophase [2, 3]. If the accumulation stage is carried out at the potential of the limiting diffusion current for ions to be determined, then there will be relationships, similar to those described above, between the ion concentration and the maximum current for dissolution of the metal. This variant, inverse voltamperometry of the metal, has been widely discussed in the literature, so that we will not consider it specially. Information on the concentration of ions in solution can be obtained, regardless of the kinetics of the electrode process used [3].

Given a Constant Current (Inverse Chronopotentiometry). The relation between potential and time is recorded, and the conversion time of the process τ_c is measured. The method has been called chronopotentiometry [4], or film chronopotentiometry with accumulation [5]. For reasons, presented by one of us previously [10], it is clearly expedient to call this variant electrochemical analysis by inverse chronopotentiometry (chronopotentiography).

The main relations between the parameters, for the process of electrodissolution of the metal at constant current, are given in Table 2. From this data, and by use of equation (2), it follows that the conversion time of the process is proportional to the concentration of electroactive ions in the solution:

$$\tau_c = \frac{nFSDC^0\tau_{de}}{\delta i}. \qquad (5)$$

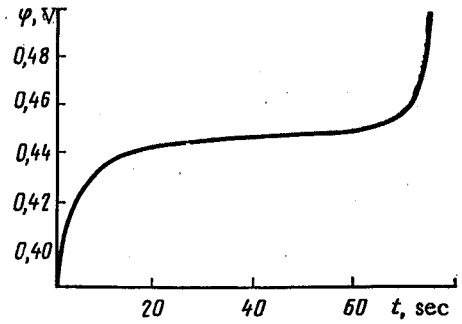

Fig. 1. Chronopotentiogram for the oxidation of silver. Supporting electrolyte M KNO_3 + HNO_3; pH 2; $[Ag^+] = 4 \cdot 10^{-4}$ g-ion/liter; $\tau_{de} = 2$ min; $i = 3 \cdot 10^{-6}$ A.

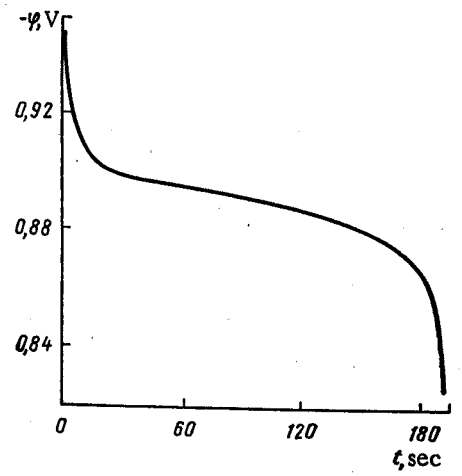

Fig. 2. Chronopotentiogram for the oxidation of cobalt. Supporting electrolyte 0.1 M K_2SO_4; $[Co^{2+}] = 3 \cdot 10^{-3}$ g-ion/liter; τ_{de} = 2 min; i = 3 $\times 10^{-5}$ A.

Equation (5) is truly independent of the kinetics of the electrode process, and of the properties of the system forming in the accumulation stage.

It is possible to obtain information on the kinetics of the electrode process from the chronopotentiograms for electrodissolution of the micro- and macrophases of the metal, together with the equations shown in Table 2. An experimental check of the equations was obtained for an example of the category: ionization of silver (reversible process) and ionization of cobalt (irreversible process).

The electrodeposition of silver was carried out at a potential of -0.6 V (relative to a silver/silver chloride electrode), and that of cobalt at -1.6 V (relative to a mercury/mercurous sulfate electrode). The working electrode was of graphite, type 1 [3, p. 46]. The power supply was from a P-5827 potentiostat. Curves relating φ and t were recorded with a KSP-4 potentiometer. The solutions were freed from surfactant material by passage through a charcoal column [3, p. 149].

Figures 1 and 2 show chronopotentiograms for the oxidation of silver and cobalt, previously deposited on a graphite electrode. Figure 3 gives the relation between φ and $-\lg\frac{C^0+\frac{2i}{nFS}\sqrt{t/\pi D}}{Q-it}$, for dissolution of the silver microphase, and between φ and $-\lg\left(C^0+\frac{2i}{nFS}\sqrt{t/\pi D}\right)$, for dissolution of the silver macrophase. Analysis of the data showed that the process $Ag \rightarrow Ag^+ + e$ was reversible. The slopes of the straight lines were 0.057 and 0.050, which are consistent with the equations given in Table 2. The value of the proportionality coefficient γ, calculated from the equation and the data of Fig. 3, was close to $5 \cdot 10^5$ C^{-1}.

Figure 4 gives the relationships between φ and $-\lg(\tau_c - t)$, and between φ and $-\lg i$, for the dissolution of cobalt. The slopes of the straight lines (1) and (2) were 0.060 and 0.050, which are consistent with the equation for an irreversible process, with βn = 1.0 to 0.8. The value of K_s was $2 \cdot 10^{-8}$ cm/sec, and γ was of the order 10^4 C^{-1}.

Figure 5 gives the relations between the conversion times for the processes of oxidation of silver and cobalt and the concentrations of these ions in the solutions. The fact that there was direct proportionality in both cases confirmed that it should be possible to use both the reversible and irreversible electrode reactions for analytical purposes.

It should be noted that inverse chronopotentiometry has a definite advantage over the normal direct variant of the method. It is well known that, in the direct variant, the conversion time for successively occurring electrode processes depends on the conversion time of the previously occurring electrode reaction [11, p. 228], i.e., on the concentration of electropositive elements in the solution. In the case of inverse chronopotentiometry, the previous process is completed at the instant that the potential for the subsequent process is reached. At any moment there is only one electrode reaction proceeding, determined by the potential, so that the conversion time for any process depends only on the quantity of the corresponding metal on the electrode.

Given a Constant Electrode Potential (Inverse Chronoamperometry). From the general point of view the problem of describing the electrodissolution of metal from the surface of an indifferent electrode, at constant potential, can be expressed as follows:

$$i = -nFSD\frac{\partial C}{\partial x}\Big|_{x=0}. \qquad (6)$$

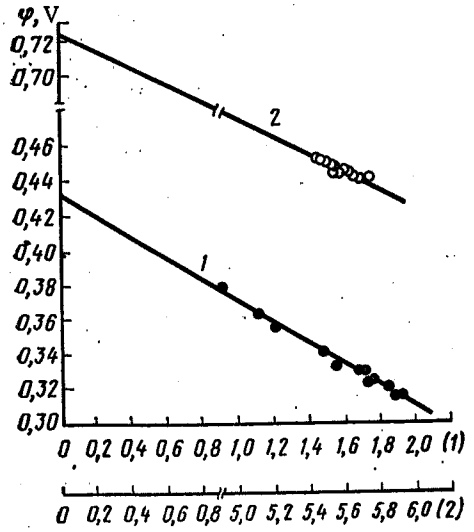

Fig. 3. Relationships between electrode potential and $-\lg \frac{C^0 + \frac{2i}{nFS}\sqrt{it/\pi D}}{Q - it}$ (curve 1), and between electrode potential and $-\lg\left(C^0 + \frac{2i}{nFS}\sqrt{it/\pi D}\right)$ for the electrodissolution of silver.

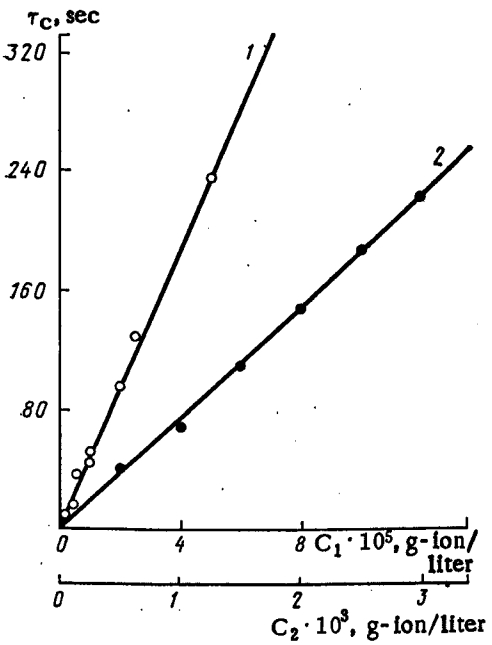

Fig. 5. Relation between conversion time and concentration of (1) silver ions and (2) cobalt ions in solution.

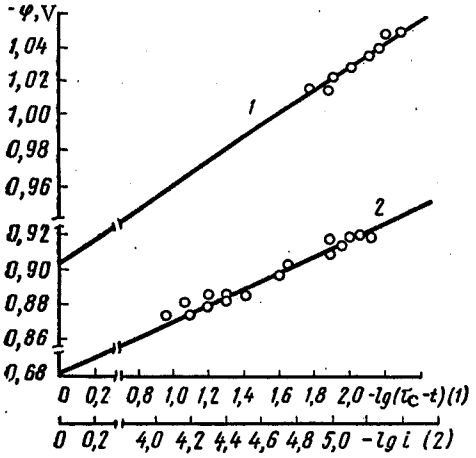

Fig. 4. Relationships between electrode potential and $-\lg(\tau_c - t)$ (curve 1) and between electrode potential and $-\lg i$ (curve 2) for the electrodissolution of cobalt.

The concentration field of electroactive ions is given by Fick's equation:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \tag{7}$$

with initial and boundary conditions:

$$C(X, 0) = C^0,$$
$$-\left.\frac{\partial C}{\partial x}\right|_{x=0} = \frac{K_S}{D}\left[a e^{\frac{\beta nF}{RT}(\varphi - \varphi^0)} - C(0,t)\, e^{\frac{-\alpha nF}{RT}(\varphi - \varphi^0)}\right], \tag{8}$$

where $a = a_\infty\left\{1 - \exp\left[-\gamma\left(Q - \int_0^t i dt\right)\right]\right\}$.

A strict solution of this problem presents known difficulties, so we will first consider the simplest case of a slow electrochemical reaction (irreversible process). Using equations (6) and (8), and neglecting the second term in equation (8), we obtain:

$$i = nFSK_S a_\infty \times \left\{1 - \exp\left[-\gamma\left(Q - \int_0^t i dt\right)\right]\right\} \exp\frac{\beta nF}{ET}(\varphi - \varphi^0). \tag{9}$$

Introducing the symbols

$$\varkappa = nFSK_S a_\infty \exp\frac{\beta nF}{RT}(\varphi - \varphi^0),$$

and

$$y = \exp\left[-\gamma\left(Q - \int_0^t i dt\right)\right],$$

TABLE 3. Relationships between the Parameters for the Process of Electrodissolution of a Metal at Constant Potential. Recorded Relation i = f(t)

Process	Reversible		Irreversible	
Equations relating the main parameters	Microphase $i=nFSD^{1/2}a_{\infty}\gamma Q \times\left(\frac{1}{\sqrt{\pi t}}-K\sqrt{D}\right) \times e^{\frac{nF}{RT}\left(\varphi-\varphi_1^0\right)}$ $i=nFSD^{1/2}a_{\infty}\gamma Q\frac{1}{\sqrt{\pi t}} \times e^{\frac{nF}{RT}\left(\varphi-\varphi_1^0\right)}$	Macrophase $i=nFSD^{1/2} \times\pi^{-1/2}t^{-1/2}A$ $A=a_{\infty}$ $\times e^{\frac{nF}{RT}\left(\varphi-\varphi_1^0\right)}$	$i=\frac{\varkappa\left(e^{\gamma Q}-1\right)}{e^{\varkappa\gamma t}+e^{\gamma Q}-1}$ $\varkappa=nFSK_S a_{\infty} e^{\frac{\beta nF}{RT}\left(\varphi-\varphi_1^0\right)}$	
			Microphase $i_{t\to 0}=\varkappa\gamma Q$	Macrophase $i_{t\to 0}=\varkappa$
Parameters of the process which can be determined	n, γ		K_S, βn, γ	
Values depending on concentration and character of the relationship	Peak current proportional to concentration	—	Peak current proportional to concentration	—

then $y' = y\gamma i$, and equation (9) can be written in the form:

$$\frac{y'}{\gamma y}=\varkappa(1-y). \tag{10}$$

Integration of this gives:

$$\ln\frac{y}{1-y}=\varkappa\gamma t-\ln\text{const}. \tag{11}$$

Using the initial condition $y=e^{-\gamma Q}$ at t = 0, we find that the constant $=e^{\gamma Q}-1$, so that

$$y=[1+(e^{\gamma Q}-1)\,e^{-\varkappa\gamma t}]^{-1}. \tag{12}$$

The expression for the current has the form:

$$i=\frac{\varkappa\left(e^{\gamma Q}-1\right)}{e^{\varkappa\gamma t}+e^{\gamma Q}-1}. \tag{13}$$

The peak current is given by:

$$i_{t\to 0}\frac{\varkappa\left(e^{\gamma Q}-1\right)}{e^{\gamma Q}}. \tag{14}$$

For dissolution of the microphase ($\gamma Q \ll 1$)

$$i_{t\to 0}=\varkappa\gamma Q. \tag{15}$$

For dissolution of the macrophase ($\gamma Q \gg 1$)

$$i_{t\to 0}=\varkappa. \tag{16}$$

It follows from equations (15) and (16) that, in the case of dissolution of microphase metal, the peak current is proportional to the quantity of metal deposited, or, taking equation (2) into account, to the concentration of the ion concerned in the solution.

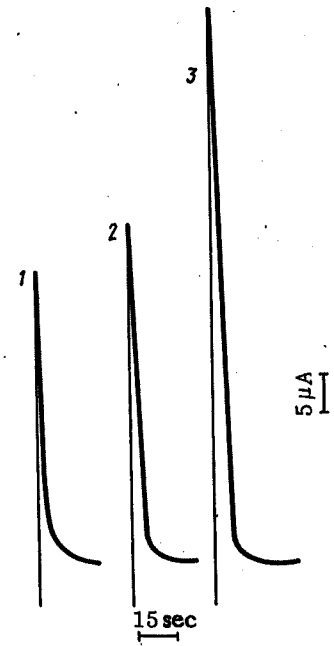

Fig. 6. Chronoamperograms for the oxidation of cobalt: Supporting electrolyte 0.1 M K_2SO_4; $[Co^{2+}]$ = $5 \cdot 10^{-4}$, $6 \cdot 10^{-4}$, and $1 \cdot 10^{-3}$ g-ion/liter for 1), 2), and 3) respectively; τ_{de} = 30 sec; dissolution potential 0.1 V.

For the case of dissolution of the macrophase, the peak current is determined only by the kinetic parameters of the process, and does not depend on the concentration of electroactive ions in the solution. Table 3 gives the fundamental relationships between the parameters for the process of electrodissolution of the metal at constant potential.

The following reasoning may be used to evaluate the nature of the relation between peak current and quantity of metal deposited on the electrode, for the case of a rapid electrode reaction.

From the moment that the dissolution potential φ is reached, the concentration of metal ions close to the electrode surface rapidly increases. The rate of the process is then determined by the rate of the act of ionization of the metal. The conversion time of the process (relaxation time) may be estimated from the nonidentity $D/K_S < \sqrt{Dt}$, so that, if $D = 10^{-5}$ cm^2/sec and $K_S = 10^{-2}$ cm/sec, $t > 0{,}1$ sec. If the quantity of metal deposited in the accumulation stage is big enough ($\gamma Q \gg 1$), then, in the course of a small elapse of time after attainment of potential φ, the quantity of metal dissolving will be small as compared with the initial quantity. Accordingly, any change in activity of the metal during the dissolution process may be neglected.

The boundary conditions for equation (7) can be expressed as follows:

$$C(0, t) = a_\infty \exp \frac{nF}{RT}(\varphi - \varphi^0) = A. \tag{17}$$

If $\varphi \gg \varphi_e$, then $A \gg C^0$.

Equations (7) and (17) have a solution of the form [12]:

$$\frac{C(x, t) - A}{C^0 - A} = \operatorname{erf}\left(\frac{x}{2\sqrt{DT}}\right). \tag{18}$$

Then an expression for the current can be obtained for the identities (6) and (18):

$$i = nFSD^{1/2}\pi^{-1/2}t^{-1/2}A, \tag{19}$$

which is correct if $t > t_r$ and $\gamma\left(Q - \int_0^t i dt\right) > 1$. From this it is clear that the current does not depend on the amount of metal deposited on the electrode, nor on the concentration of metal ions in the solution.

In the case of dissolution of the metal microphase ($\gamma Q \ll 1$), the boundary condition for equation (7) can be written in the form:

$$C(0, t) = L + K \int_0^t D \left.\frac{\partial C}{\partial x}\right|_{x=0} d\tau, \tag{20}$$

where

$$L = a_\infty \gamma Q \exp \frac{nF}{RT}\left(\varphi - \varphi_1^0\right);$$

$$K = \gamma nFSa_\infty \exp \frac{nF}{RT}\left(\varphi - \varphi_1^0\right);$$

$$C(x, t) \underset{x \to \infty}{=} C^0; \quad C(x\ 0) = C^0.$$

Equation (20) is correct if $t > D/K_S^2$. Then, applying a Laplace transformation to equations (7) and (20), we obtain an expression for the flow of metal ions:

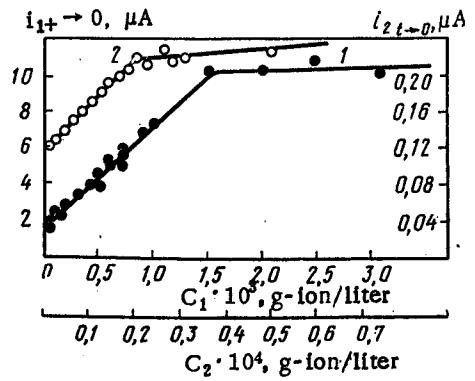

Fig. 7. The relation between the peak current and the concentration of 1) cobalt ion, and 2) silver ion in the solution.

$$-D\left.\frac{\partial C}{\partial x}\right|_{x=0} = \sqrt{D}\,(L - C^0)\left[\frac{1}{\sqrt{\pi t}} - K\sqrt{D}\times e^{K^2Dt}\,\mathrm{erfs}\,(K\sqrt{Dt})\right]; \quad (21)$$

$$K\sqrt{D}e^{K^2Dt}\,\mathrm{erfc}\,(K\sqrt{Dt}) = \begin{cases} K\sqrt{D} & \text{at } t = 0 \\ 0 & \text{at } K\sqrt{Dt} > 2. \end{cases}$$

The relation between the current and the process parameters, under the above stated limiting conditions, is given by the equations:

$$i = nFSD^{1/2}a_{\infty}\gamma Q\left(\frac{1}{\sqrt{\pi t}} - K\sqrt{D}\right) \times \exp\frac{nF}{RT}\left(\varphi - \varphi_1^0\right); \quad (22)$$

$$i = nFSD^{1/2}a_{\infty}\gamma Q\,\frac{1}{\sqrt{\pi t}} \times \exp\frac{nF}{RT}\left(\varphi - \varphi_1^0\right). \quad (23)$$

It is clear from these equations that, in the case of dissolution of a metal microphase, the current is proportional to the quantity of metal deposited on the electrode, or, since identity (2) applies, to the concentration of the corresponding metal ion in solution.

Thus, information as to the concentration of ions in solution can be obtained from the analysis of inverse chronoamperograms only in the particular case of dissolution of metal microphase. The absence of a relation between current and the amount of metal deposited on the electrode in other cases (macrophase metal) makes the method as described unsuitable for analytical pruposes. Polarization of the electrode at constant potential can evidently be used for analysis only in its coulometric variant.

The above conclusions were compared with experimental data, using as examples the discharge of silver (reversible process) and of cobalt (irreversible process). The electrodeposition of silver was carried out at $\varphi = -0.6$ V, and of cobalt at -1.6 V (mercury/mercurous sulfate electrode). Electrodissolution was carried out at $+0.1$ V for silver, and -0.8 V for cobalt. The magnitude of the peak current was measured with a KSP-4 potentiometer for cobalt, and with an M95 low-inertia microammeter for silver.

Figure 6 shows the relation between current and time for the electrodissolution of cobalt. Figure 7 shows the relationships between the corresponding peak currents and the concentrations of Ag^+ and Co^{2+} ions in solution. Over the concentration ranges $2 \cdot 10^{-6}$ to $2 \cdot 10^{-5}$ g-ion/liter for silver, and $5 \cdot 10^{-5}$ to $1.5 \cdot 10^{-3}$ g-ion/liter for cobalt, the peak current was proportional to the concentration of the corresponding ion. But, when the concentration was increased, the peak current became independent of the concentration of electroactive ion in solution.

This agreement between theory and experiment confirms the view, expressed above, that it is impossible to determine the concentration from the value of the current observed at constant electrode potential. However, if we take into account equation (2), and assume that the anodic process is carried out to complete dissolution of the metal from the electrode surface, we would expect a proportional relationship between the quantity of electricity passing in the anodic stage and the concentration of the corresponding metal ion in the solution. In this case it is possible to make use of coulometric measurement.

Comparison of the Sensitivities of Determination for Various Electrode Polarization Conditions

The main factor restricting the sensitivity of determination is the capacity current. We can calculate the value of the capacity current term in the measurement, for various electrode polarization conditions.

The value of the capacity current is given by the equation:

$$i_C = \frac{dQ_C}{dt}. \quad (24)$$

In the case of a linear change in potential with time, the above equation can be rewritten in the form:

$$i_C = S\,\frac{d\varepsilon}{d\varphi}\cdot\frac{d\varphi}{dt} + \varepsilon\,\frac{d\varepsilon}{dt}, \quad (25)$$

where $d\varphi/dt = V$, $d\varphi/dt = C_d$.

When S = const,

$$i_C = SVC_d. \tag{26}$$

Using the equations presented in Table 1, we can obtain for the reverse process:

$$\frac{i_C}{I} = \frac{C_d\delta}{11{,}6n^2FDC^0\tau_{de}}. \tag{27}$$

For $C_d = 20\ \mu F/cm^2$, $\delta = 10^{-3}$ cm, n = 1, $D = 10^{-5}$ cm^2/sec, and $\tau_{de} = 1800$ sec, we obtain $i_C/I = 0.5$ at $C^0_{min} = 2\cdot10^{-12}$ g-ion/cm^3 = $2\cdot10^{-9}$ g-ion/liter.

Calculations by Zakharov [5], at given constant current conditions, showed that $C^0_{min} = 1.15\cdot10^{-8}$ g-ion/liter for the following experimental conditions: $C_d = 20\ \mu F/cm^2$; $\Delta\varphi = 0.1$ V; $\delta = 1\cdot10^{-3}$ om; $D = 1\cdot10^{-5}$ cm^2/sec; $\tau_{de} = 1800$ sec; n = 2.

When the coulometric variant is used, at a given constant potential, the condition that $Q_C \leq 0.1\,Q$ should be fulfilled. We may write approximately that $Q_C = C_d(\varphi_{el}-\varphi)S$, or with $\Delta\varphi = 0.5$ V, then $Q_C/Q = 0.1$, with $C^0_{min} = 5\cdot10^{-11}$ g-ion/cm^3 = $5\cdot10^{-8}$ g-ion/liter.

From the above analysis it follows that, in electrochemical analysis, the optimum conditions for concentration are achieved either at a constant electrode potential corresponding to the limiting diffusion current of the ion to be determined or at a constant current greater than the limiting diffusion current. Information on the concentration of ions in solution can be obtained either from the analysis of polarization curves for the dissolution of metal, recorded using a potential which alters linearly with time, or from chronopotentiograms recorded with a given current. Recording the current at a given constant electrode potential in the dissolution stage gives information on the concentration of the solution only in particular cases. The coulometric variant of this procedure can be used in analytical chemistry. Information on the kinetics of the electrode process can be obtained under all conditions of electrode polarization.

The advantage of inverse chronopotentiometry is the existence of a proportional relation between a measurable value (the conversion time) and the concentration of the ion to be determined in the solution. The slope of the straight line, with coordinates τ_C and C^0, remains constant over a wide range of concentration, and does not depend on the kinetics of the electrode process.

The maximum sensitivity for determination can be achieved by polarizing the electrode at a potential which varies linearly with time (inverse voltamperometry).

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