# THE THEORY OF THE ELECTROLYTIC DISSOLUTION OF FILMS FROM THE SURFACE OF AN INDIFFERENT ELECTRODE

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Papers by a number of authors have dealt with the problems of the electrolytic dissolution of films of metal [1-3] and various compounds formed by the electrode material [3, 4] and have also discussed the possibility of using these phenomena in polarography.

We have now obtained experimental data on the electrolytic dissolution of films of sparingly soluble compounds formed by the products of the electrode reation with a special component of the solution. We have observed certain characteristic relationships which make it possible to use the formation of precipitates of insoluble compounds on an electrode as a method of concentrating ions in polarographic analysis [5]. Since the method can be used in practice for analytical purposes and to study the kinetics of certain chemical and electrochemical reactions, it is of interest to make a theoretical examination of the electrolytic dissolution of such films. This problem is examined in the present paper. The conclusions reached are compared with experiment for the case of the system $2Tl^+ + 6OH^-/Tl_2O_3 \cdot nH_2O + 2e$.

The processes resulting in the formation of a film (1st stage) and its dissolution (2nd stage) can be represented in general form as follows:

$$\left.\begin{aligned} &M^{n+} \rightarrow M^{(n+m)} + me, \\ &pM^{(n+m)+} + (n+m)\,A^{p-} \rightarrow M_pA_{n+m} \end{aligned}\right\} \text{1st stage} \quad (1), (2)$$

$$\left.\begin{aligned} &M_pA_{n+m} \underset{k_2'}{\overset{k_1}{\rightleftarrows}} pM^{(n+m)+} + (n+m)\,A^{p-}, \\ &M^{(n+m)+} + me \rightarrow M^{n+}. \end{aligned}\right\} \text{2nd stage} \quad (3), (4)$$

Here, $M^{n+}$ and $M^{(n+m)+}$ represent the different valence states of the M ions, and $A^{p-}$ represents the substance forming a sparingly soluble compound with $M^{(n+m)+}$ ions. Equations (1)-(4) describe the anodic process of deposit formation and the cathodic process of electrolytic dissolution of the deposit. The reverse electrode processes can be represented in analogous fashion.

Let us examine the case where $p = 1$. If an excess of substance $A^-$ is present, its concentration can be included in the effective rate constant, which we shall denote $k_2$ ($k_2 = k_2'[A^-]^{(n+m)}$). The process of electrolytic dissolution is then described by the differential equations

$$D\frac{\partial^2 C_1}{\partial x^2} + k_1C_2 - k_2C_1 = 0; \quad (5)$$

$$\frac{\partial C_2}{\partial t} = k_2C_1 - k_1C_2 \quad (6)$$

with the following initial and boundary conditions:

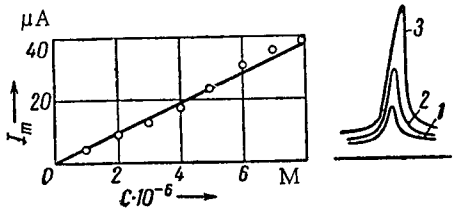


Fig. 1. Relationship between the maximum current for the electrolytic dissolution of a $Tl_2O_3 \cdot nH_2O$ film deposited on a graphite electrode ($\varphi_{el}$ = +1.0 V relative to a saturated calomel electrode) from a solution of 0.2 N $NH_4OH$ + 0.2 N $NH_4Cl$ (pH 9.5) of a period of two minutes on the $Tl^+$ ion concentration in the solution, together with the corresponding polarization curves. 1) $3 \cdot 10^{-6}$ M $Tl^+$; 2) $5 \cdot 10^{-6}$ M $Tl^+$; 3) $8 \cdot 10^{-6}$ M $Tl^+$.

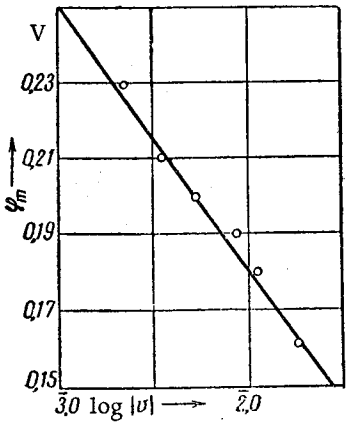


Fig. 2. Relationship between the potential of the maximum on the polarization curve and the logarithm of the rate of change of the electrode potential; the electrolytic deposition of the thallium film was carried out for two min from a solution of 0.2 N $NH_4Cl$ + 0.2 N $NH_4OH$ (pH 9.5) at a potential of +1.0 V relative to a saturated calomel electrode.

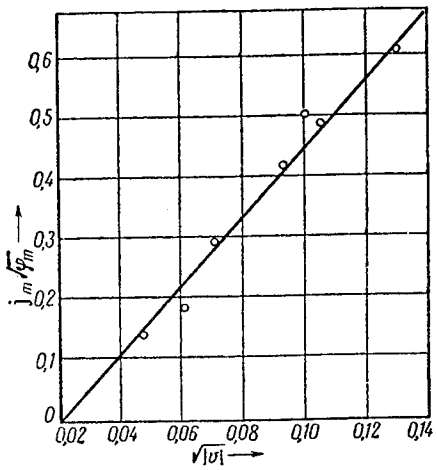


Fig. 3. Relationship between $j_m\sqrt{\varphi}_m$ and $\sqrt{v}$; the experimental conditions are given in the caption to Fig. 2.

$$C_2'(x, 0) = C_2^2, \quad C_1(x, 0) = \frac{C_2^0}{\sigma};$$

$$\left(\frac{\partial C_1}{\partial x}\right)_{x=0} = C_1(0, t)\, ke^{Bvt}; \quad \left(\frac{\partial C_1}{\partial x}\right)_{x=l} = 0. \quad (7)$$

Here, $C_1$ and $C_2$ are the concentrations of the substances $M^{(n+m)}$ and $MpA_{n+m}$; $k_1$ and $k_2$ are the rate constants of the forward and back chemical reactions; $\sigma = (k_2)/k_1$; $l$ equals the thickness of the film; $B = -\alpha nF/RT$; $k = \frac{k_s}{D_1} \exp\left[-\frac{\alpha nF}{RT}(\varphi_1 - \varphi^0)\right]$ for the cathodic process; $B = \frac{\beta nF}{RT}$, $k = \frac{k_s}{D_2} \exp\left[\frac{\beta nE}{RT}(\varphi_1 - \varphi^0)\right]$ for the anodic process; $\varphi^0$ is the standard potential of the system; v the rate of change in potential during the electrolytic dissolution cycle; t is the duration of the electrolytic dissolution; and $\varphi = vt$ is the electrode potential measured from the initial potential $\varphi_1$.

In Eq. (5) the derivative of the concentration with respect to time has been omitted, since in the case of rapid chemical reactions* ($k_1 t, k_2 t \gg 1$), equilibrium is established between the chemical reactions and the diffusion process [6]. Equation (6) does not contain a term describing the diffusion of the solid substance $M_pA_{n+m}$ since its diffusion can be neglected.

The boundary conditions reflect the fact that the $M^{(n+m)+}$ ions taking part in the electrode process do not enter the film from outside, their concentration gradient at the electrode surface being proportional to the electrolytic dissolution current.

If the thickness of the film is much greater than the quantity $\mu_2 = \sqrt{D/k_2}$ ($\mu_2$) is the thickness of the reaction layer [7]) it is not difficult, by transforming (5) to (7) by Laplace's method, to obtain the following expression for

* It should be noted that only the case of rapid chemical reactions is of interest, since a sufficiently high rate of formation of the deposit is a necessary condition for concentration.

the transformed value of the flow of substance $M^{(n+m)+}$ close to the electrode surface:

$$\frac{\partial \bar{C}_1(p)}{\partial x}\Big|_{x=0} = \frac{C_2^0}{\sigma\mu_2}\frac{1}{p}\sqrt{\frac{p}{p+k_1}} - \frac{1}{k\mu_2}\sqrt{\frac{p}{p+k_2}}\frac{\partial \bar{C}_1(p+Bv)}{\partial x}\Big|_{x=0}, \tag{8}$$

where p is the transformation coefficient.

From (8) by means of the theorem of convolution, we obtain an integral equation for the electrolytic reduction current density

$$j(t) = nFD\frac{\partial C_1}{\partial x}\Big|_{x=0}:$$

$$j(t) = \frac{nFDC_2^0}{\sigma}\frac{ke^{-k_1t/2}I_0(k_1t/2)}{k\mu_2 + e^{-Bvt}} +$$

$$\frac{k_1e^{-kt/2}}{2(k\mu_2 + e^{-Bvt})}\int_0^t e^{-Bv\tau}e^{k_1\tau/2}j(\tau)\left[I_0\left(\frac{k_1(t-\tau)}{2}\right) - I_1\left(\frac{k_1(t-\tau)}{2}\right)\right]d\tau. \tag{9}$$

For the case $k_1 \gg B_v$ the approximate solution of this equation can be written in the form

$$j(t) = \frac{pFDC_2^0}{\sigma}\frac{ke^{-k_1t/2}e^{Bvt}I_0(k_1t/2)}{k\mu_2e^{Bvt} + e^{-k_1t/2}I_0(k_1t/2)}. \tag{10}$$

Direct substitution of relationship (10) in Eq. (9) and numerical integration show that in the case of sufficiently rapid chemical reactions ($k_1t \gg 1$ and $k\mu_2 \leq 1$) Eq. (9) is satisfied with high accuracy.

Expanding the Bessel functions into an asymptotic series, we obtain the following simple expression for the electrolytic dissolution current density:

$$j(t) = \frac{nFDC_2^0}{\sigma}\frac{ke^{Bvt}}{(k\mu_2e^{Bvt}\sqrt{\pi k_1t} + 1)}. \tag{11}$$

By differentiating Eq. (11) with respect to time we can readily find the potential $\varphi_m$ at which the current reaches its maximum value:

$$\frac{k\mu_2\sqrt{\pi k_1}}{2B\sqrt{v}} = \sqrt{\varphi_m}e^{-B\varphi m}. \tag{12}$$

By combining Eqs. (11) and (12) we obtain an expression for the maximum electrolytic dissolution current

$$j_m = \frac{nFDC_2^0}{\sigma\mu_2}\frac{\sqrt{v}}{\sqrt{\pi k_1\varphi_m}(1 + 1/2B\varphi_m)}, \tag{13}$$

which, since $\sigma = \sigma'/f_2$ [$\sigma'$ is the thermodynamic equilibrium constant for the chemical reaction (9)] and it is assumed that $1/2B\varphi_m \ll 1$, we can be readily represented in the form

$$j_m = \frac{C_2^0f_2}{\sigma'\mu_2}\frac{\sqrt{v}}{\sqrt{\pi k_1\varphi_m}}. \tag{14}$$

Formula (14) contains the activity of the deposit $a_2^0 = C_2^0f_2$. A natural assumption is that at low film thickness the activity is proportional to the quantity of substance in the film and the latter is proportional to the concentration of ions in the solution and the duration of the electrolytic deposition. Application of the Nernst equation with allowance for this proportionality made it possible to obtain a relationship between the equilibrium potential of the $Bi^{III}/Bi^0$ system and the duration of the electrolytic deposition, which showed good agreement with experiment [10].

Using the relationships given above, we obtain an expression for the maximum electrolytic dissolution current in the form

$$j_m = \frac{k'_d C\tau}{\sigma\mu_2} \frac{\sqrt{v}}{\sqrt{\pi k_1 \varphi_m}}, \quad (15)$$

where C is the concentration of $M^{n+}$ ions in the solution; $\tau$ is the duration of the electrolytic deposition; and $k'_d$ is a proportionality coefficient.

The experimentally observed relationship between the maximum current for the electrolytic dissolution of a $Tl_2O_3 \cdot nH_2O$ film and the concentration of $Tl^+$ ions in solution is given in Fig. 1. The relationship shows a direct proportionality, which is in agreement with Eq. (15). This leads to the important practical conclusion that the process of concentration of ions in the form of thin films of sparingly soluble compounds, with subsequent recording of the currents for the electrolytic dissolution of the resulting deposits, can be used for the determination of ions of variable valence present in solution in extremely low concentrations.

Let us now compare the experimentally observed relationships between $\varphi_m$ and $j_m$ and the rate of change of potential v with formula (12) and (14) or (15). By writing Eq. (12) in the form

$$\varphi_m = \frac{2,3}{2B} \log \varphi_m - \frac{2,3}{B} \log \frac{k\mu_2 \sqrt{\pi k_1}}{2B} + \frac{2,3}{2B} \lg v, \quad (16)$$

we can readily show that the relationship $\varphi_m = f(\log v)$ at high values of $B\varphi_m$ should be almost linear.

The corresponding experimentally observed relationship for the electrolytic reduction of a $Tl_2O_3 \cdot nH_2O$ film is shown in Fig. 2. In accordance with Eq. (12), this relationship is expressed by an almost straight line with slope equal to $-0.071$, which corresponds to a value of $\alpha = 0.2$.

It follows from Eq. (14) that a linear relationship exists between $j_m\sqrt{\varphi_m}$ and $\sqrt{v}$ at high values of $B\varphi_m$. It can be seen from Fig. 3 that the experimental data show good agreement with the theoretical conclusions.

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