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THE EFFECT OF ELECTROLYSIS POTENTIAL ON THE DEPTH OF THE ANODIC WAVE IN THE METHOD OF AMALGAM POLAROGRAPHY WITH A STATIONARY DROP ELECTRODE

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The relation between depth of anodic wave and electrolysis potential has been investigated. The theoretical relations derived agreed well with experimental data obtained for gallium and indium in supporting electrolytes of 0.1 M KCl + 0.1 M Na salicylate, and 0.25 M KOH + 0.5 M EDTA respectively. The reason was established for the decrease in anodic wave height when the electrolysis potential was increased in the negative direction.

It is well known that the depth of the anodic in amalgam polarography at a stationary mercury electrode depends on the potential used for the preliminary electrolysis. Experiments by various workers have led to contradictory results as to the nature of this dependence [1-3].

We have derived a theoretical expression for the relation between depth of anodic wave and electrolysis potential, and have been able to explain the experimental facts. In deducing the required expression we considered that impoverishment of metal ions in the solution during the preliminary electrolysis is practically negligible (within a precision of 5%), so that their concentration in the solution can be taken as constant* with a precision of 5%.

The electrode process is practically irreversible, so that the rate of the reverse process, i.e., ionization of the metal, during the preliminary electrolysis can be neglected.

Experiments showed that the depth I of the anodic wave was proportional to the concentration C_2 of metal atoms in the amalgam:

$$I = K'C_2. \tag{1}$$

Assuming a uniform distribution of metal in the mercury drop at the end of the electrolysis [5, 6], and taking the above condition into consideration, we have:

$$C_2 = \frac{i_e \cdot \tau}{zFV_2}. \tag{2}$$

Here i_e is the electrolysis current; τ is the electrolysis time; V_2 is the volume of the mercury drop.

From (1) and (2) it can be shown that:

$$I = Ki_e; \quad K = \frac{K'\tau}{zFV_2}. \tag{3}$$

It is clear that the constant K does not depend on the electrolysis potential.

Preliminary electrolysis into the stationary mercury drop was carried out with a stirred solution, i.e., under stationary diffusion conditions. Under these conditions the relation between potential and current is given by the equation for a completely irreversible polarographic wave [7]:

$$\varphi = \varphi_{1/2} - \frac{b}{\alpha} \lg \frac{i_e}{i_e^x - i_e}, \tag{4}$$

* No impoverishment of the solution was observed when the dimensionless parameter $b > 3$. This corresponded to definite values for the duration of electrolysis, the volume of solution, and the dimensions of the mercury drop [4].

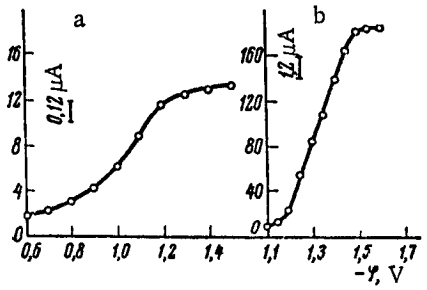

Fig. 1. Cathodic polarograms at a dropping mercury electrode: a) For gallium in 0.1 M KCl + 0.1 M Na salicylate (pH = 4); b) for indium in 0.25 M KOH + 0.5 M EDTA.

$$\varphi_{1/2} = \varphi_{eq} - \frac{b}{\alpha} \lg \frac{i_e^x}{i_0}. \qquad (5)$$

Here $\varphi_{1/2}$ is the half-wave potential; φ_{eq} is the equilibrium potential; i_e^x is the limiting electrolysis current; α is the transfer coefficient; $b = 2.3\ RT/zF$; i_0 is the exchange current.*

From Eqs. (4) and (5) we can obtain the required relation between depth of anodic wave and electrolysis potential:

$$\varphi = \varphi_{1/2} - \frac{b}{\alpha} \lg \frac{I}{I^x - I} \qquad (6)$$

or

$$I = \frac{I^x}{e^{\frac{\alpha}{b'}(\varphi - \varphi_{1/2})} + 1}, \qquad (7)$$

where $b' = RT/zF$; I^x is the limiting constant value for the depth of the anodic wave, corresponding to the limiting value of the electrolysis current ($I^x = Ki_e^x$).

It is clear from Eqs. (6) and (7) that, under the two conditions taken above, the relation between the anodic wave depth and the electrolysis potential will be expressed by a curve completely analogous to that of a fully irreversible polarographic wave.

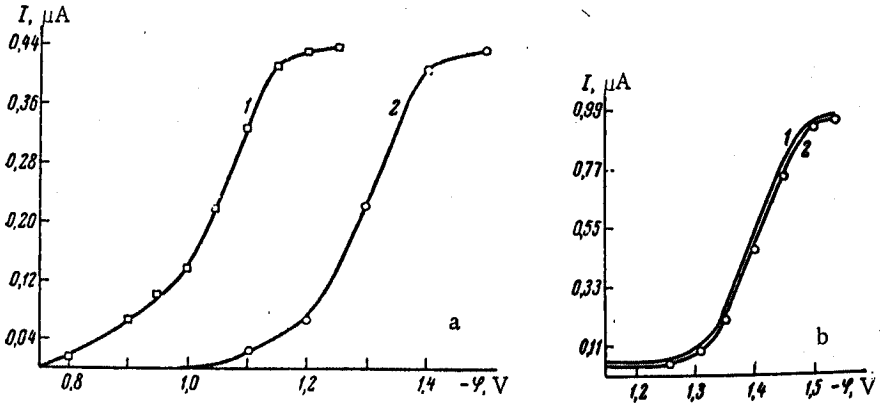

Fig. 2. 1) Theoretical and 2) experimental curves relating anodic current and electrolysis potential (τ = 5 min; d_k = 0.1 cm; V_{sol} = 5 ml): a) For gallium amalgam with a supporting electrolyte of 0.1 M KCl + 0.1 M Na salicylate (pH = 4); b) for indium amalgam with a supporting electrolyte of 0.25 M KOH + 0.5 M EDTA. The solution concentrations were 10^{-4} M gallium and 10^{-5} M indium.

It might be presumed that, with a changing concentration of metal in the mercury drop during the electrolysis process, and with changes in the equilibrium potential φ_{eq} and the exchange current i_0 in conformity with Eqs. (4) and (5), there would also be changes in the half-wave potential and in the electrolysis current at constant potential. However, it is easily shown that these fears are groundless. From the theory of delayed discharge ionization we have the following expression for the exchange current:

$$i_0 = K_I \cdot e_1 e^{-\alpha\varphi_{eq}/b'} \qquad (8)$$

* In the electrolysis process, as the concentration of metal atoms in the amalgam changes there are corresponding changes in the equilibrium potential φ_{eq} and in the exchange current i_0. However, it will be shown below that the half-wave potential remains constant during this process.

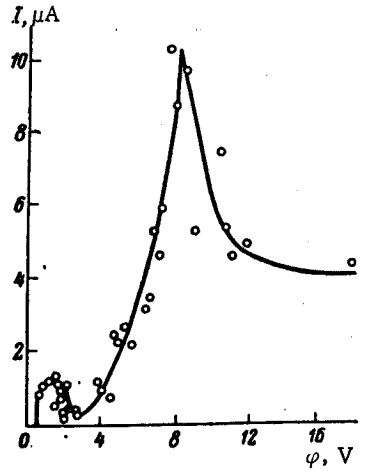

Fig. 3. The effect of electrolysis potential on the anodic current of lead amalgam: supporting electrolyte 0.1 M KCl; τ = 5 min; d_K = 0.08 cm; V_{sol} = 5 ml. The concentration of lead in the solution was 10^{-5} M.

or

$$\varphi_{eq} + \frac{b}{\alpha} \lg i_0 = \frac{b}{\alpha} \lg K_1 \cdot C, \tag{9}$$

where K_1 is the velocity constant for the discharge process at zero potential.

Solving Eqs. (5) and (9) simultaneously, we have:

$$\varphi_{1/2} = \frac{b}{\alpha} \lg \frac{K_1 C_1}{i_e^x}. \tag{10}$$

The electrolysis current is proportional to the concentration of ions in the solution:

$$i_e^x = K_1^x C_1, \tag{11}$$

where K_1^x is the proportionality constant for the limiting electrolysis current, which does not depend on the potential. From Eqs. (10) and (11) we have:

$$\varphi_{1/2} = \frac{b}{\alpha} \lg \frac{K_1}{K_1^x}. \tag{12}$$

It follows from Eq. (12) that the half-wave potential (for a fully irreversible electrode process) will not depend on the concentration of metal ions in the solution nor on the concentration of metal atoms in the amalgam.

The relation between anodic wave depth and electrolysis potential, over the range where there was no reduction of the supporting electrolyte ions, was investigated theoretically and experimentally for gallium and indium.

The theoretical investigation of the relation $I = f(\varphi)$ was carried out by means of Eq. (7). It was necessary to know the cathodic half-wave potential $\varphi_{1/2}$ and the transfer coefficient α to determine these, we obtained cathodic polarograms for gallium and indium at a dropping mercury electrode (Fig. 1). In both cases the cathodic half-wave potentials were derived from these by constructing lines with coordinates $\log[I_k/(I_k - i)]$ and φ. Here I_k and i respectively are the limiting current and the current at potential φ for the cathodic polarogram at a dropping mercury electrode. The intersection of this straight line with the axis of the ordinate $\log[I_k/(I_k - i)]$ gave the value of $\varphi_{1/2}$.

The transfer coefficient α was calculated from the equation $\alpha = b/b_k$, where $b = 2.3\,RT/zF$ and b_k is the slope of the curve with coordinate $\log[I_k/(I_k - 1)]$ and φ. The values of α for indium and gallium were found to be 0.117 and 0.066 respectively.

The present state of the theory of amalgam polarography with accumulation did not enable us to calculate the limiting value of the anodic wave depth I^x, so that the latter was determined experimentally. Values of I were calculated from the values obtained for $\varphi_{1/2}$, α, and I^x at different values of φ.

Figure 2 shows the curves of $I = f(\varphi)$ for gallium and indium; the experimental curves had the form predicted by Eq. (7). For indium the theoretical and experimental curves for $I = f(\varphi)$ practically coincided, but for gallium the theoretical curve lay at more positive potentials than the experimental curve. This difference can be explained as follows: the rate of a strongly irreversible electrode process, such as the reduction of gallium, is very slow near the equilibrium potential, and only becomes significant at more negative potentials.

There are statements in the literature [2, 3] that the anodic wave depth is reduced if the potential of the final rise on the polarogram is exceeded during electrolysis. It has been stated that this phenomenon can be explained by the reduction in electrode potential caused by a considerable increase in the value of iR for the electrolytic cell. However, our investigations have shown that, under the experimental conditions, the value of iR does not exceed 0.01 V and, consequently, cannot explain the considerable decrease in anodic wave depth. An obvious explanation of the phenomenon is that the electrode becomes screened by bubbles of evolved hydrogen.

A further increase in the electrolysis potential* (Fig. 3), in the negative direction, led to an increase in the anodic wave depth. The explanation of this is that increasing the electrolysis potential caused a more vigorous hydrogen evolution, and the resulting energetic stirring of the solution led to a decrease in the thickness of the diffusion layer at the electrode. This resulted in an increased rate of reduction of the metal ions at the mercury drop, and hence to an increase in the anodic wave depth. Stirring the solution, to remove hydrogen bubbles, has been used by some workers to increase the sensitivity for determination of microimpurities by the method of oscillographic polarography after accumulation [8-10].

At still higher negative potentials there was a decrease in the anodic wave depth, attributable to excessive evolution of hydrogen, which formed a gas film round the electrode and thus prevented the access of fresh portions of solution containing depolarizer.

Thus, for the potential range in which there was no reduction of supporting electrolyte ion, the relation $I = f(\varphi)$ was described by Eqs. (6) and (7). The first part of the curve in Fig. 3, from about −0.4 to −1.2 V, was given by Eq. (7). At more negative potentials, where reduction of supporting electrolyte ions occurred, the relation $I = f(\varphi)$ became more complicated, and was largely determined by the nature of the supporting electrolyte.

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*Electrolysis at potentials more negative than −4.0 V was carried out using a rectifier.