THE EFFECT OF THE VOLUME OF THE SOLUTION ON THE DEPTH OF THE ANODE INDENTATION IN AMALGAM POLAROGRAPHY

(UDC 543)

A. G. Stromberg and A. A. Kaplin

(Tomsk Polytechnic Institute)

Translated from Zavodskaya Laboratoriya, Vol. 30, No. 5,
pp. 525-527, May, 1964

The relation between the depth of the anode indentation in amalgam polarography and the solution's volume has been investigated; a method has been developed for the graphical determination of the rate constant of electrolysis. It has been established that screening the upper half of the mercury drop during electrolysis gives an electrolysis rate constant whose value is only half that of the calculated one.

The essential feature of amalgam polarography [1, 2] is preliminary electrolytic accumulation of the determined element on a stationary mercury drop at a regulatable potential, followed by anode dissolution of the amalgam (with recording of the anode dissolution current). The depth of the anode indentation is proportional to the concentration of the determined ion in the solution. However, the effect of the volume of the solution, the duration of preliminary electrolysis and the radius of the mercury drop on the depth of the anode indentation has not been closely investigated hitherto.

In [3] we derived a theoretical relation between the depth of the anode indentation and various factors, which (provided the size of the mercury drop is constant) is as follows:

$$I_a = a\left(1 - e^{-b}\right), \tag{1}$$

where

$$a = K_2 C_1^0 V; \quad b = \frac{K_1}{zF} \cdot \frac{t}{V}. \tag{2}$$

Here, I_a is the depth of the anode indentation, μa ; C_1^0 is the initial ionic concentration in the solution, mmole/liter; V is the volume of the working solution, ml; t is the duration of preliminary electrolysis, sec; z is the number of electrons participating in the electrode reaction; F is the Faraday number; $K_2 = \frac{K_2^1}{V_d}$; K_1 and K_2' are constants in the equations:

$$I_e = K_1 C_1^0 \quad \text{и} \quad I_a = K_2' C_a. \tag{3}$$

Here, I_e is the preliminary electroysis current, μa ; C_a is the concentration of the metal in the amalgam, mmole/liter; V_d is the volume of the drop, ml.

K_1 and K_2' are proportional to the surface of the mercury drop; further, K_1 depnds on the mixing intensity of the solution.

We will write equation (1) as follows:

$$I_a = a'V\left(1 - e^{-\frac{b'}{V}}\right), \tag{4}$$

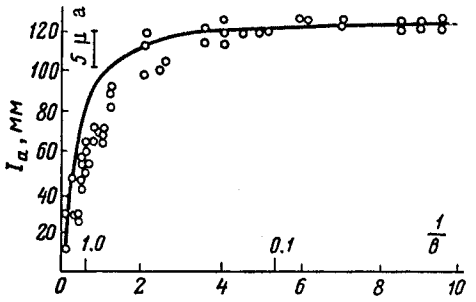

Fig. 1. Depth of anode indentation versus solution volume (I_a, V). Preliminary electrolysis potential -1.0 V (rel. to a sat. c.e.); galvanometer sensitivity 0.282 μ a/mm. The curve was plotted from equations (1)-(4), with $K_1 = 60$ and $K_2 = 1280$ A. mole^{-1} cm^{-3}.

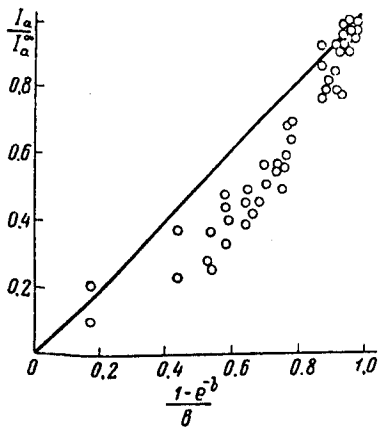

Fig. 2. Depth of anode indentation versus solution volume (I_a/I_a and $1-e^{-b}/b$). For experimental conditions, see Fig. 1.

where

$$a' = K_2 C_1^0 \qquad b' = \frac{K_1}{zF} \cdot t. \tag{5}$$

From equation (4), it may be seen that, other factors being equal (t, r, C_1^0) there is a complicated relation between the depth of the anode indentation and the volume of the working solution. Fig. 1 gives a plot of I_a versus V(or $\frac{1}{b}$ and Fig. 2 a plot of $\frac{I_a}{I_a^\infty}$ versus $\frac{1-e^{-b}}{b}$ (I_a is the depth of the anode indentation where $b < 0.1$, i.e. where the electrolysis time is low and the volume of solution high).

At a constant initial concentration of the ions reduced on the electrode, the theoretical relation between the depth of the anode indentation and solution volume was quantitatively confirmed by our experimental data. We used an electrolyzer with quartz insertion beakers of different size [4] and a device allowing the position of the mercury drop in the solution to be changed.

A magnetic stirrer was used for mixing, together with a current of oxygen-free nitrogen. The above mentioned relations are only correct where mixing is constant, the rate of this being monitored in our experiments by recording the initial electrolysis current.* The mixing rate varies with changing the speed of the stirrer, the rate of the nitrogen feed and the position of the mercury drop within the working volume until the same initial value of the electrolysis current is obtained in all experiments. After the measurement has been carried out, the investigated solution is discharged from the beaker, and fresh previously prepared lead solution of constant concentration ($5 \cdot 10^{-5}$ mole/liter), prepared in 0.1 N KOH, is added to the beaker.

We investigated a series of working solutions (volume 0.1-10 ml) at a constant electrolysis time (30 minutes) and mercury drop size of 0.04 cm. From Fig. 1 and 2, it may be seen that the experimental points lie satisfactorily on the theoretical curve.

For graphical determination of K_1, employing equation (1) we first calculate the ratio between the depths of the anode indentations at volumes corresponding to 'b' values of 0.25, 1 and 3, e.g. V/4, V and 3V. In this case the ratio is 0.37 : 1 : 1.33. Then the value of V satisfying this condition is found on the graph (see Fig. 1). This value corresponds to b = 1 and b' = V from equations (2) and (5). The desired value of K_1 is calculated from equation (6):

$$I_a^\infty = I_a'/0.63,$$

where I'_a is the depth of the anode indentation at b = 1.

*In practice, the electrolysis current is determined one minute after commencement of electrolysis. At higher values of b (b > 1; V < 0.6 ml) this current virtually coincides with the initial current; at low values of b (b < V > 0.6 ml), by preliminary calculation from equation (3) is determined the agreement between the current I_e one minute after electrolysis and the initial current I_e^0 from the equation $I = I_e^0 e^{-b}$.

The slight scatter of the experimental data is due to variations in the mixing rate during preliminary electrolysis.

The value of K_1, determined from the electrolysis current by (3), is 31 A. mole^{-1} · cm^3, i.e. approximately half the value determined from Fig. 1. A similar ratio between both K_1 constants was observed when an experimental check was made of the theoretical relation between the depth of the anode indentation and the preliminary electrolysis time [5], evidently due to screening of the upper half of the mercury drop during preliminary electrolysis.

Therefore, to compare the values of the K_1 constants found from the graph and from the electrolysis current, the value of the later must be doubled.

We will now consider the two limiting cases of ionic concentration of the solution after preliminary electrolysis [3]. With b < 0.1 (large volume of working solution) equation (1) become:

$$I_a^{\infty} = ab = a'V \cdot \frac{b'}{V} - a'b'. \qquad (6)$$

Equation (6) will be correct where, at completion of electrolysis, the concentration of the determined ions in the solution has become constant ($C_1 > 0.95\, C_1^0$). In this case the depth of the anode indentation will be independent of the volume of the solution.

Substituting in the equation for b (equation (2)) the values of z and F, and the experimentally determined values of K_1 and t, we obtain

$$b = \frac{60 \cdot 1800}{2 \cdot 96\,500} = \frac{0.57}{V},$$

$$\text{Therefore } V = \frac{0.57}{b}.$$

In our case the depth of the anode indentation is, therefore, virtually independent of the volume of the solution where V > 6 mm. With b > 3 (small volume of the working solution, all other factors being constant) equation (1) becomes

$$I_a^0 = a = a'V. \qquad (7)$$

Equation (7) will be correct in a case where, at completion of electrolysis, the concentration of the determined ions in the solution virtually zero ($C < 0.05\, C_1^0$). In this case the depth of the anode indentation is directly proportional to the volume of the working solution. For our conditions, equation (7) will be correct with $V \leq 0.19$ ml. The investigation of the relation between the depth of anode indentation and electrolysis time for a volume of 0.1 ml showed that virtually all the metal is deposited from this volume in 30 minutes.

Therefore, the experimental data fully confirm the theoretical conclusions and allow one to determine the best volume for determining the given concentration of the element. In particular, under our experimental conditions it is undersirable to increase the volume of the solution to more than 5 ml. On the other hand, for the same sample weight* a reduction in the volume of the working solution does not lead to a marked increase in the sensitivity of the method, because in small volumes the depth of the indentation (other things being constant) is reduced as a result of exhaustion of the solution. Hence, under our conditions a reduction in the solution's volume from 2 to 0.2 ml increased the sensitivity by only 4 times, not 10 times, because at the same concentration the depth of the indentation in 2 ml is 2.5 times greater than in 0.2 ml (the values of b being 0.28 and 2.8 respectively).

LITERATURE CITED

1. A. G. Stromberg and E. A. Stromberg, Zavodskaya laboratoriya, 27, 3 (1961).
2. Z. Kublik, Wiadom. Chem., 8, 499 (1961).
3. A. G. Stromberg, Izv. SO AN SSSR, 5, 76 (1962).

*This corresponds to constancy of the product $C_1^0 V$, i.e. the increase in the concentration of metal ions in the solution is proportional to the reduction in the volume.

4. A. G. Stromberg, M. S. Zakharov, A. A. Kaplin, V. I. Kuleshov, and V. S. Smorodinov. Collection: Spectral and Chemical Methods of Analysis [in Russian], Izd-vo Metallurgiya (1964).
5. A. G. Stromberg and M. S. Zakharov, Collection: Methods of Analysis of Chemical Reagents and Preparations [in Russian], (1963), p. 16.

All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.
