POLAROGRAPHY OF METALS ON A GRAPHITE ELECTRODE

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Cathodic polarograms of Au, Ag, Hg, Sb, Sn, Pb, Bi, Cu, Cd, In, Ga, Tl, Co, and Ni ions and anodic polarization curves of the electrodissolution of Fe, Mn, Zn, and Ge as well as the other metals listed above were obtained by using a graphite indicator electrode. The possibility of determining traces of 16 metals by the film-polarography method was demonstrated and the conditions required for this process were selected.

The application of various types of graphite electrodes in the cathodic and anodic polarography of metals have been described in a number of papers. In general, conditions for determining ions of individual metals in a narrow range of concentrations have been presented. We have now studied the cathodic and anodic (film) polarography of the ions of metals reduced to the elementary state in an aqueous medium on a specially prepared graphite electrode.

We used an oscillographic polarograph of the 02-TsLA type and an ON-101 recording system (Hungary). The indicator electrode was a graphite electrode prepared as described earlier in [1]. Saturated calomel electrodes were used as auxiliaries. Oxygen was removed from the solutions with a current of nitrogen. During electrodeposition, the solutions were stirred with a magnetic stirrer, or else a rotating electrode was used. The anodic polarization curves were recorded in a solution at rest.

Depending on the hydrodynamic conditions and the kinetics of the electrode process, the cathodic polarograms had the form of a wave or a curve containing a maximum (for a linearly varying potential). The first occurred if the solution was stirred during the recording of the curves or if the electrode reaction was irreversible. This may be seen from the polarograms of mercury and nickel (Fig. 1), respectively.

In the case of a reversible process, the cathodic polarograms recorded in an undisturbed solution show a current maximum if the natural convection does not make up the loss of electrically active ions in the layer next to the electrode. An example of such curves is provided by the polarograms of gold. The limiting cathode current is in all cases proportional to the concentration of metal ions in solution.

In agreement with theory [2] and earlier-published experimental data, the anodic curves of all the metals contain a sharp maximum. The value of the maximum electrodissolution current, as might be expected, depends on the potential of the electrode in the stage of the electrodeposition of the metal. Displacement of the potential in the negative direction is accompanied by an increase in the maximum anode current, up to a certain specific value. After this the value remains constant if no new electrode process begins (for example, the discharge of hydrogen ions) on further raising the cathodic polarization. If such a process does take place, there is a certain fall in the electrodissolution current. This is clearly a natural consequence of the fall in the amount of deposited metal resulting from the screening of the electrode surface by the evolving hydrogen.

This effect may be to a considerable extent removed if a disc electrode revolving at a high speed is employed. Thus, manganese and zinc ions are discharged on a graphite electrode in parallel with hydrogen ions. For this reason the cathodic polarograms of these metals cannot be obtained. On a rotating electrode, however, these metals are well concentrated and may be determined from the electrodissolution current of the deposit.

Theoretical consideration of the electrodissolution of a metal with a linearly varying potential [2] shows that the nature of the relationship between the maximum anode current and the concentration of metal ions in solution changes on passing from thin to thick [3] metal films. The ratio of the maximum electrodissolution current of a

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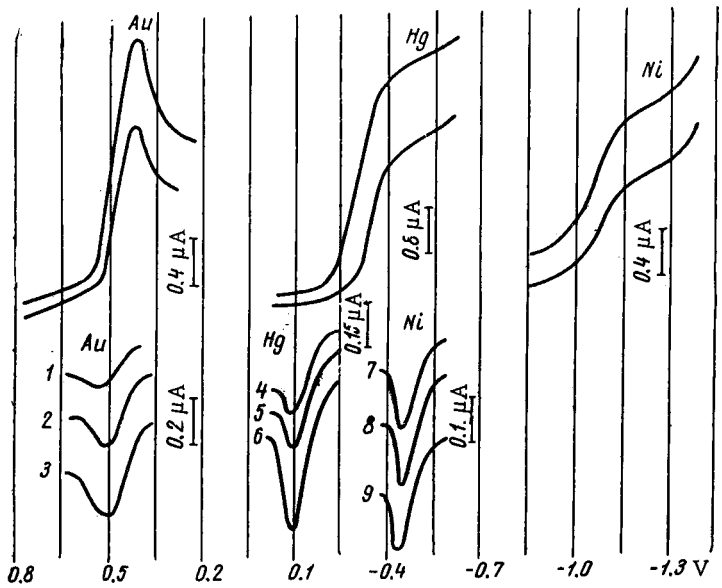

Fig. 1. Cathodic polarization curves of gold, mercury, and nickel (1 and $1.5 \cdot 10^{-4}$ g-ion/liter in 1M HCl, 1M KSCN, and 0.1M NH_4Cl + 0.1M NH_4OH, respectively) and electrodissolution curves of the same metals concentrated for 1 min from solutions containing $2 \cdot 10^{-6}$ g-ion/liter Au (III), Hg (II), or Ni (II). Potentials of electrodeposition 0.2 (1), 0.0 (2), −0.2 (3), −0.3 (4), −0.4 (5), −0.6 (6), −1.1 (7), −1.2 (8), and −1.3 V (9).

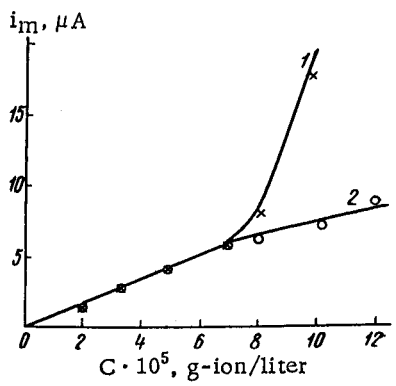

Fig. 2. Maximum electrodissolution current of nickel as a function of the concentration of nickel ions in 0.1M NH_4OH + 3M NH_4Cl, using (1) a three-electrode and (2) a two-electrode polarograph arrangement. Duration of electrodeposition, 1 min at potential −1.2 V. Rate of change of voltage 0.02 V/sec.

thick metal film to the original quantity on the electrode exceeds the corresponding ratio for thin films by a factor of 3.2 in the case of a reversible process of electrodissolution in an undisturbed solution and by a factor of 2.3 in the case of an irreversible process. On increasing the amount of the metal on the electrode and also its dissolution current, a linear variation of the voltage applied to the cell by means of an ordinary polarograph is incapable of ensuring a linear variation in the potential of the working electrode with time.

The fall in the rate of change of potential takes place as a result of the ohmic voltage drop in the solution and in the measuring resistance, and as a result of the so-called nonideal polarizability of the electrode. The influence of the first two factors was considered by Delahay [4], and the last becomes obvious if we remember that, after deposition of a thick film of metal on an indifferent electrode, the electrolyzer behaves as a galvanic cell connected to an external current source. The fall in the rate of change of the electrode potential during electrodissolution of the metal, which may be determined by means of an ÉPPV1-M1 potentiometer, is accompanied by a reduction in the maximum current and a distortion of the form of the polarization curve [5].

The effect in question is removed by using a three-electrode arrangement of the polarograph with a voltage-drop compensator, for example, a 02-TsLA. Thanks to the feedback and the compensator, the voltage applied to the cell varies in such a way that the rate of change of electrode potential remains constant, even for quite large currents (up to 50 or 100 μA).

Figure 2 shows the maximum electrodissolution current of nickel as a function of the concentration of the corresponding ions in solution. Both two- and three-electrode arrangements of the oscillographic polarograph were used. We see from the figure that the maximum anode current (< 6 μA) is proportional to the concentration of nickel

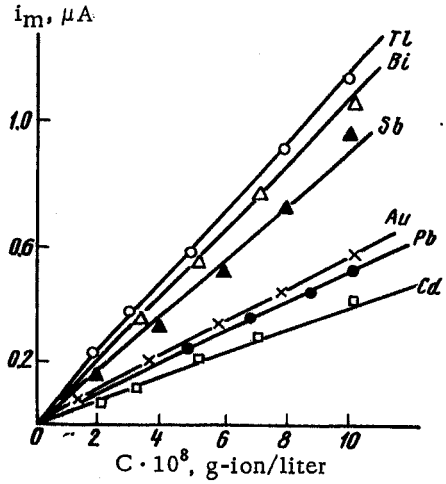

Fig. 3. Maximum electrodissolution current of metals as a function of the concentration of their ions in solution: τ_{el} = 10 min, v = 0.017 V/sec.

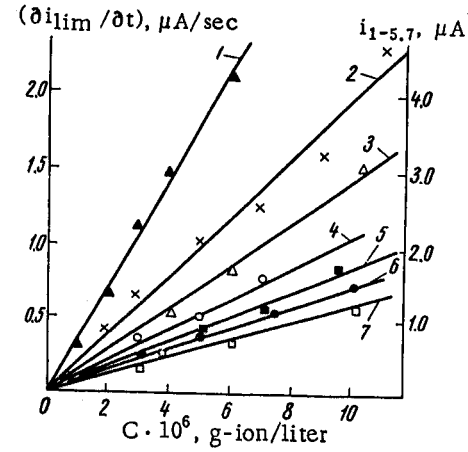

Fig. 4. Maximum electrodissolution current of Fe (1), Co (2), Hg (3), Zn (4), Ni (5), Mn (6), In (7) as a function of the concentration of their ions in solution: τ_{el} = 5 min (1, 2, 4), 3 min (6), 2 min (3), and 1 min (5, 7).

ions in solution. At higher concentrations of the electrically active ions, when using the voltage drop compensator, the slope of the curve $i_m = f(c)$ becomes greater than that of the initial rectilinear part. On operating with the two-electrode arrangement, the slope diminishes. This fact must be taken into account when recording the electrodissolution curves of fairly large quantities of metal.

A direct proportionality between the maximum anode current and the concentration of metal ions in solution occurs when using the ordinary polarograph over the concentration range $1 \cdot 10^{-8}$ to $1 \cdot 10^{-5}$ g-ion/liter for an electrodeposition period of ≤ 1-2 min and a voltage rate of change ≤ 0.02 V/sec.

Figures 3 and 4 show the maximum electrodissolution current of a number of metals as a function of their concentration in solution. In all cases the $i_m = f(c)$ relationship is directly proportional, which enables us to use the method of film polarography for determining minute traces of these elements.

The relation between the maximum electrodissolution current of metals and the period of electrodeposition has almost the same character as the relation between the maximum electrodissolution current and the concentration of metal ions in solution. In practice, the relation is of a directly proportional nature for electrodeposition periods between 1 and 30 min if the concentration of metal ions in solution is $1 \cdot 10^{-6}$ g-ion/liter.

The table shows the potentials of the cathodic-reduction halfwave (for concentrations $1 \cdot 10^{-4}$ to $1 \cdot 10^{-5}$ g-ion/liter), the potentials of electrodeposition, and the potentials of the electrooxidation current maxima of a number of metals (v = 0.017 V/sec) associated with their determination on a graphite electrode. We see from the table that electrode processes involving, for example, copper, may take place (depending on the nature of the solution) between 0 and −1.6 V. Cobalt is deposited on a graphite electrode from solutions containing SO_4^{2-}, SCN^-, or NH_4^+ ions at potentials of −1.4 V in the first and −1.2 V in the second and third cases; the corresponding anodic curves occur in the potential range −0.6-0.0 V. In practice, dissolution of copper takes place in the same potential range in the solutions indicated. The use of a different base electrolyte (1N NaOH + 1N NaSCN) enables us to separate these processes ($\varphi_m(Cu) = -0.45$ V, $\varphi_m(Co) = -0.70$ V). The precipitation of iron on the electrode from solutions in which it exists in the form of hydroxyl ions is impeded by the intensive discharge of hydrogen ions. However, concentration of the metal may be effected from a neutral or alkaline medium by introducing a compound preventing the hydrolysis of the iron ions into the solution. Sharp polarograms of the electrodissolution of iron are established by using a 0.05M solution of potassium sulfosalicylate (pH = 5). Electrodeposition is effected in this case at a potential of −1.6 V on a rotating electrode. The electrodissolution of iron in a 0.1M solution of sodium tartrate or citrate (pH = 10) is described by a polarization curve with two current maxima, which is apparently due to the intermediate formation of a film of iron hydroxide (II) on the electrode. The oxidation of iron in a more alkaline tartrate solution is described by a polarization curve with one current maximum. This base electrolyte is the most suitable for determining small quantities of iron.

Characteristics of the Polarographic Determination of Metal Ions on a Graphite Electrode

Metal ion	Base electrolyte	$\varphi_{1/2}$, V	φ, V	φ_m, V
Au (III)	1-M HCl	+0.5	—0.2	+0.5
	1-M KNO_3	+0.75	—0.2	+0.85
Ag (I)	0.1-M KNO_3	+0.05	—0.2	+0.30
Cu (II)	1-M KNO_3	—0.37	—0.6	—0.05
	0,02-M $H_{tartr.}$ + 0.02-M		—0.8	—0.4
	NH_4Cl + KOH, pH = 9			
	1-M KOH + 0.1-M $H_{tartr.}$		—1.6	—0.5
	1-M KOH + 1-M NaSCN		—1.3	—0.45
	0.1-M NH_4Cl	—0.2	—0.5	—0.15
Bi (III)	0.1-M KCl + 0.1-M HCl	—0.20	—0.4	—0.05
	0.1-M NH_4Cl	—0.2	—0.4	—0.1
Pb (II)	0.1-M HCl	—0.55	—0.8	—0.55
	0.1-M NH_4Cl, pH = 4	—0.6	—0.8	—0.55
	20% $H_{citr.}$		—0.8	—0.55
Sb (III)	1-M NH_4AC	—0.3	—1.0	—0.25
	1-M HCl	—0.25	—0.5	—0.05
Sn (IV)	1-M NH_4Cl	—0.75	—1.2	—0.50
	1-M HCl		—1.2	—0.50
	20% $H_{citr.}$		—1.2	—0.25
Cd (II)	0.1-M HCl	—0.8	—1.2	—0.75
	1-M KCl		—1.2	—0.70
Hg (II)	1-M KSCN	—0.25	—0.6	—0.1
	0.1-M KNO_3	+0.2	—0.4	+0.5
In (III)	1-M NH_4SCN	—0.9	—1.4	—0.7
	0.2-M KCl, pH = 4	—0.9	—1.3	—0.65
Tl (I)	0.2-M $(NH_4)_2SO_4$ + NH_4OH, pH = 8	—0.95	—1.4	—0.9
Ni (II)	0.1-M NaSCN	—1.1	—1.2	—0.4
	0.1-M NH_4OH + 0.1-M NH_4Cl		—1.2	—0.5
	1-M KNO_3 + 0.01-M HNO_3		—1.2	—0.1
Co (II)	0.1-M NaSCN	—1.1	—1.2	—0.45
	0.2-M NH_4OH		—1.2	—0.4
	0.1-M K_2SO_4		—1.4	—0.1
	1-M KOH + 0.1-M $H_{tartr.}$		—1.6	—0.6
	1-M KOH + 1-M NaSCN		—1.2	—0.7
Fe (III)	1-M KOH + 0.01-M $H_{tartr.}$		—1.4	—0.85
	0.05-M $Na_{sulfosal.}$ pH = 5		—1.6	—0.55
Zn (II)	0.1-M KOH		—1.6	—1.35
Mn (II)	1-M KOH + 0.1-M $H_{tartr.}$ + 0.1-M hydrazine sulfate		—2.0	+0.1

Electrode processes involving gold are displaced in the direction of negative potentials on replacing potassium chloride in solution. In the case of nickel, the introduction into the solution of certain compounds capable of combining the metal ions into complexes is accompanied by a considerable displacement of the cathodic and anodic curves along the potential axis and a fall in the potential difference of the halfwave (or the potential of electrodeposition, taken at the beginning of the plateau of the limiting diffusion current) and the potential of the anodic peak indicates that the discharge and ionization of copper in all base electrolytes (except ammonium chloride) and the corresponding processes for tin, nickel, cobalt, iron, zinc, and manganese are irreversible.

Of all the metals here studied, only gallium and germanium give poor anodic curves. The cathodic polarograms of gallium ions on base electrolytes of 1M KNO_3, pH = 5, or 1M KSCN are quite clear; we have not been able to obtain the corresponding curves for germanium.

It follows from the foregoing discussion that the graphite electrode may successfully be used both in the cathodic and anodic (film) polarography for a large number of metals, enabling the metal ions to be determined over an extremely wide range of concentrations ($1 \cdot 10^{-8}$ to 10^{-3} g-ion/liter).

The indifference and chemical stability of the electrode (wide working range of potentials) enables it to reveal electrode processes representing the reduction and oxidation of both noble and fairly electronegative elements. The concentration of the elements in the form of deposits on the solid electrode makes it possible to determine metals which are poorly soluble in mercury. The sensitivity of determination ($1 \cdot 10^{-8}$ g-ion/liter) may be increased on using vector polarography [6] or the difference [7] variant of the method.

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