MECHANISM OF THE ANODIC DISSOLUTION OF INDIUM AMALGAM IN ACID SOLUTIONS

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Abstract

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MECHANISM OF THE ANODIC DISSOLUTION OF INDIUM AMALGAM IN ACID SOLUTIONS

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The dissolution of metals in solutions of high acidity in the absence of oxygen occurs as a result of the independent course of two coupled electrochemical reactions—the anodic process of metal ionization and the cathodic process of hydrogen evolution ([1]). The increase, usually observed under these conditions, in the rate of dissolution of metals with decreasing pH is generally explained by an increase in the rate of the cathodic process, which leads to a shift of the stationary potential of the metal in the positive direction and causes, as a secondary effect, an increase in the rate of the anodic process. As for the kinetics of the anodic process proper, at first glance, in sufficiently acid solutions in which passivation of the metal does not occur, the rate of the process of metal ionization at a given potential should not depend on the acidity of the solution. Meanwhile, the results of polarization measurements on an iron electrode in solutions of $HClO_4 + NaClO_4$, obtained in the work of Bonhoeffer and Heusler ([2]), indicate that the rate of anodic dissolution of iron at a given potential decreases strongly with increasing acidity over a broad pH interval (0–4)*. An analogous effect is observed in the anodic dissolution of nickel ([4]).

Since the question of the influence of pH on the rate of the anodic process of metal ionization is of essential importance for understanding the mechanism of this process, we have studied the influence of solution acidity on the kinetics of the anodic and cathodic processes on an electrode of indium amalgam, **which is distinguished by a low value of the exchange current** ([5])*. By combining polarization measurements with radiochemical measurements on a stationary amalgam electrode ([5],[7]), we studied the dependence of the anodic and cathodic processes and of the exchange current on the acidity of the solution (from $9.5 \cdot 10^{-4}$ M to 3.3 M $HClO_4$) on 0.1 M indium amalgam in a solution of 0.01 M $In(ClO_4)_3$ with additions of $NaClO_4$ to maintain constant ionic strength ($3M$), with vigorous stirring of the amalgam and the solution.

Figure 1 shows the dependence of the rate of the true anodic process i_a (found by the radiochemical method using radioactive—

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* The authors explained this effect by the catalytic influence of hydroxyl ions on the process of anodic dissolution of iron; in doing so they relied on the results of the work of Kabanov and Leykis (^{1},^{3}), who showed that hydroxyl ions participate in the rate-limiting stage of the process of anodic dissolution of iron in alkaline solutions.

** The use of an amalgam electrode in a solution of a salt of the metal of the same name makes it possible to study the influence of pH not only on the anodic dissolution of the metal, but also on the kinetics of the corresponding reverse process—the discharge of metal ions. In addition, this eliminates the influence of the hydrogen-evolution process, which in the case of iron and nickel electrodes may be adsorbed on the metal surface and affect the kinetics of the anodic process.

*** In addition, polarographic data (^{6}) show that the discharge wave of indium ions becomes more reversible with increasing pH, and it could be expected that, in the region of the equilibrium potential as well, the kinetics of the ionization-discharge process would depend on pH.

isotope In^{114}) on the potential, along with the usual polarization curves measured by current. A linear dependence is observed between the potential and $\lg i_a$, and the slope coefficient of the anodic curve $(\varphi, \lg i_a)$ is practically independent of the acid concentration and is $b_a = 0.027$ V, which corresponds to a transfer coefficient $\beta = 2.2$ (^{5}). As can be seen, as the acid concentration increases from $9.5 \cdot 10^{-4}$ M to 0.5 M, the exchange current i_0 decreases by a factor of 500 (from $1 \cdot 10^{-3}$ to $2 \cdot 10^{-6}$ A/cm^2).

Figure 2 presents anodic and cathodic polarization curves for solutions of different acidity. In order to quantitatively estimate the effect of the $HClO_4$ concentration on the rate of the anodic process, a dashed straight line is drawn in Fig. 2a at the potential $\varphi = -0.250$ V; the points of intersection of the anodic curves with this line are the values of i_a at constant potential. Figure 3 shows the dependence of the values of i_a obtained in this way on the $HClO_4$ concentration.* In the $HClO_4$ concentration interval (C) $5 \cdot 10^{-3}$–0.2 M, the dependence $(\lg i_a, \lg C)$ is rectilinear, with slope coefficient $p = -1.12$; at $C > 0.2$ M the rate of the anodic process is practically independent of acidity. In the same Fig. 3 are plotted the values of the exchange currents i_0 (found by the radiochemical method) for $C < 0.1$ M, i.e., for the interval of $HClO_4$ concentrations in which the equilibrium potential of the amalgam is independent of acidity; the slope of the straight line $(\lg i_0, \lg C)$ is $p = -0.99$. Since at equilibrium $i_0 = i_a = i_k$, where i_k is the rate of the true cathodic process, this means that the rates of the anodic and cathodic processes at the equilibrium potential are inversely proportional to the concentration of $HClO_4$.** This conclusion is in satisfactory agreement with the result of determining the dependence of i_a on C at $\varphi = -0.250$ V. If we take into account the linear dependence observed by us between φ and $\lg i_a$, as well as the presence of proportionality between i_a and the concentration of the amalgam at $\varphi = \text{const}$ (^{5}), then for $C < 0.1$ M our experimental data can be represented by the equation:

Fig. 1

Figure 1: Fig. 1

$$i_a = k[\mathrm{In}][\mathrm{H}^+]^{-1} e^{3\varphi F/RT}, \tag{1}$$

where $\beta = 2.2$.

More complex is the dependence of the cathodic process on acidity. As can be seen from Fig. 2b, throughout the entire range of $HClO_4$ concentrations, strong inhibition of the cathodic process is observed with increasing acidity. The slope of the cathodic curves is very high (0.40 V) and gradually decreases when the potential is shifted in the negative direction. It was shown earlier (^{5}) that, in acidified $In(ClO_4)_3$ solution, with appreciable displacement from the equilibrium potential in the negative direction, the usual polarization curves do not correspond to the stage of discharge of indium ions, but apparently reflect the presence of some chemical reaction in solution preceding this stage.

Fig. 1. Dependence of the true anodic curves $(1', 2', 3')$, along with polarization curves $(1, 2, 3)$, on the acid concentration (1 and $1'$–$9.5 \cdot 10^{-4}$ M; 2 and $2'$–0.016 M; 3 and $3'$–0.5 M $HClO_4$).

* Since a considerable scatter of the experimental data was observed, Fig. 3 includes not only the points from Fig. 2, but also the values of i_a at $\varphi = -0.250$ V for other experiments.

** At $C < 2 \cdot 10^{-3}$ M, the results of measurements of i_a and i_k are distorted owing to strong hydrolysis and the formation of $In(OH)_3$.

In interpreting the results we have obtained, it is necessary to take into account the great tendency of indium ions toward hydrolysis:

$$\mathrm{In(H_2O)_6^{3+} + H_2O \rightleftarrows In(H_2O)_5OH^{2+} + H_3O^+}. \tag{2}$$

Using literature data for the hydrolysis constant of indium salts,* it is possible to calculate the fraction of hydrolyzed indium ions in solution under our conditions. Thus, at $C = 2 \cdot 10^{-3}$ M $HClO_4$, the fraction of $In(H_2O)_5OH^{2+}$ ions is approximately 1.5%; at $C = 1.6 \cdot 10^{-2}$ M–0.3%,

Fig. 2. Dependence of anodic (a) and cathodic (b) polarization curves on acid concentration: 1 $-2 \cdot 10^{-3}$ M for (a) and $9.5 \cdot 10^{-4}$ M for (b); 2 $-7.7 \cdot 10^{-3}$ M; 3 -0.016 M; 4 -0.05 M; 5 -0.1 M; 6 -0.5 M; 7 -1.3 M; 8 -3.3 M $HClO_4$.

and at $C = 0.1$ M it decreases to 0.05%. It may be assumed that the electrode process involves not the predominant cations $In(H_2O)_6^{3+}$ in solution, but partially hydrolyzed indium ions:

Fig. 2. Dependence of anodic (a) and cathodic (b) polarization curves on acid concentration: 1 $-2 \cdot 10^{-3}$ M for (a) and $9.5 \cdot 10^{-4}$ M for (b); 2 $-7.7 \cdot 10^{-3}$ M; 3 -0.016 M; 4 -0.05 M; 5 -0.1 M; 6 -0.5 M; 7 -1.3 M; 8 -3.3 M $HClO_4$.

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$$\mathrm{In} + 5\mathrm{H_2O} + \mathrm{OH^-} \rightleftarrows \mathrm{In(H_2O)_5OH^{2+}} + 3\mathrm{e}. \tag{3}$$

In this case the rate of the anodic process should be expressed by the equation

$$i_a = k'[\mathrm{In}][\mathrm{OH^-}]e^{\beta\varphi F/RT} = k' K_w [\mathrm{In}](\mathrm{H_3O^+})^{-1} e^{\beta\varphi F/RT}, \tag{4}$$

where $K_w = [\mathrm{H_3O^+}][\mathrm{OH^-}]$, which agrees with our experimental data (see equation 1). The expression for the rate of the cathodic process should have the form:

$$i_k = k''[\mathrm{In(H_2O)_5OH^{2+}}]e^{-\alpha\varphi F/RT} = k'' K_h [\mathrm{In(H_2O)_6^{3+}}][\mathrm{H_3O^+}]^{-1} e^{-\alpha\varphi F/RT}.$$

This equation agrees with the results of determining the dependence of the exchange current at $\varphi = \mathrm{const}$ on the concentration of $HClO_4$ (Fig. 3) and with data on the dependence of the exchange current on the concentration of the amalgam (5). The unusually high slope of the cathodic polarization curves is apparently due to the fact that, at sufficiently high current densities, the cathodic process begins to be limited by the rate of the preceding reaction of formation of hydrolyzed indium ions (equation 2). Evidently, this reaction proceeds slowly both in the bulk of the solution and on the surface of the amalgam, and therefore, when the electrode potential is shifted in the negative direction, its rate increases because of an increase in the concentration of adsorbed indium ions.**

* For a $3M$ $NaClO_4$ solution, $K_h = [\mathrm{In(H_2O)_5OH^{2+}}][\mathrm{H_3O^+}]/[\mathrm{In(H_2O)_6^{3+}}] = 10^{-4.4}$, (8).

** The assumptions we adopted concerning the participation of hydrolyzed indium ions in the electrode process and the slowness of the reaction of their formation agree with the results of measurements of the capacitance of a mercury electrode in solutions with different pH containing trivalent lanthanum ions (9): it turned out that the basic lanthanum ions arising as a result of hydrolysis have a greater adsorption capacity than simple La^{3+} cations, and the hydrolysis process proceeds on the mercury surface with a finite rate.

Fig. 3. Dependence of the rate of the anodic process i_a (a) at $\varphi = -0.250$ V and of the exchange current i_0 (b) on the concentration of $HClO_4$

Figure 3: Fig. 3. Dependence of the rate of the anodic process i_a (a) at $\varphi = -0.250$ V and of the exchange current i_0 (b) on the concentration of $HClO_4$

The question arises: why does the formation and discharge of hydrolyzed indium species proceed much more readily than the corresponding electrode processes for the simple ions $In(H_2O)_6^{3+}$ that predominate in solution? Apparently, the hydroxyl ion, like certain other anions (^{7}), is capable of serving as a kind of "bridge" facilitating electron transfer between the electrode surface and the reacting species.*

Comparison of the results we obtained with the regularities mentioned earlier for iron and nickel (^{2,4}) indicates the substantial role of hydrolyzed metal ions in the electrode process. The main difficulty arising in interpreting these results is that the participation of hydroxyl ions in the anodic process is assumed (see equation 3). Meanwhile, an approximate calculation (^{13}) shows that the bulk concentration of hydroxyl ions in acid solutions is too small to ensure the occurrence of the anodic process. It was suggested (^{2}) that, owing to the greater adsorption capacity of OH^- ions, the equilibrium

$$H_2O \rightleftharpoons H^+ + OH^-_{ads}$$

at the metal surface is shifted to the right, and therefore the surface concentration of OH^- ions considerably exceeds the bulk concentration. Another explanation seems to us more probable: if one accepts that the electrode processes of formation and discharge of multicharged metal cations proceed stepwise, by successive removal and, respectively, attachment of electrons—which is quite probable in the case of indium (^{5})—then it is natural to allow that the metal ions of lower valence formed in this process are also capable of hydrolysis. For indium it was shown that the limiting stage of the electrode process is the removal of the last electron (^{5}); consequently, this stage may be preceded by hydrolysis of the divalent indium ion

$$In(H_2O)_m^{2+} + H_2O \rightleftharpoons In(H_2O)_{m-1}OH^+ + H_3O^+,$$

and then the limiting stage will be expressed by the equation

$$In(H_2O)_{m-1}OH^+ + lH_2O \rightleftharpoons In(H_2O)_{m+l-1}OH^{2+} + e,$$

where $m + l = 6$. It is not difficult to show that in this case also the rate of the anodic process is still described by equation (4).

Fig. 3. Dependence of the rate of the anodic process i_a (a) at $\varphi = -0.250$ V and of the exchange current i_0 (b) on the concentration of $HClO_4$

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* An analogous catalytic action of OH^- ions is also observed in the polarographic reduction of certain other multicharged cations ([10,11]) and in homogeneous isotopic exchange between cations ([12]).

Note: Figure translations are in progress. See original paper for figures.