

# *Electrochemical behaviour of indium in H<sub>2</sub>SO<sub>4</sub>*

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The kinetics of the electrodisolution of indium and the hydrogen evolution on indium in H<sub>2</sub>SO<sub>4</sub> of various pH values have been investigated. For electrodisolution, Tafel slopes of 22 mV per decade and a reaction order of 1 with respect to OH<sup>-</sup> have been obtained. For hydrogen evolution, Tafel slopes were 120 mV per decade; the reaction was first order with respect to H<sup>+</sup>. An electrodisolution mechanism based on three consecutive one-electron transfer steps with the last electron transfer step rate-determining is consistent with the experimental results.

## 1. Introduction

There have been a number of studies of the anodic dissolution of indium and indium amalgams. Most of this work has been in connection with the investigation of the In/In(III) redox reaction so that acidic solutions containing In(III) have been used. Budov and Losev [1] and Visco [2] have reported that the electrodisolution of indium in HClO<sub>4</sub> followed a mechanism which consisted of three consecutive one-electron transfer steps with the formation of In(I) as the first step. The existence of In(I) in the bulk solution has been confirmed by Pichel'nikov and Losev [3], Visco [1] and subsequently by Miller and Visco [4] in more detailed studies with rotating ring-disks.

Losev and Molodov [5], who studied anodic dissolution in perchloric acid containing In(III), reported anodic Tafel slopes of 27 mV per decade and reaction orders with respect to OH<sup>-</sup> of 1.1 for HClO<sub>4</sub> ≤ 0.2 M and zero for HClO<sub>4</sub> > 0.2 M. In a later study [6] they have shown that both sulfate and chloride ions accelerate the anodic dissolution of indium in acid perchlorate supporting electrolyte. Lovrecek and Markovac [7, 8] studied the In/In(III) couple in acidic sulfate solutions and proposed a three one-electron step mechanism with a disproportionation reaction step.

In studies of the hydrogen evolution reaction on indium in 0.1 M HClO<sub>4</sub>, Butler and Dienst [9] obtained a Tafel slope of 120 mV per decade and an exchange current density of 10<sup>-11</sup> A cm<sup>-2</sup>. They concluded from their results that hydrogen ion discharge is the rate determining step. In the

course of their work, it was found that prolonged cathodic polarization was required to reduce the incipient oxide film on the indium electrode and to remove the residual dissolved oxygen in the solution in order to obtain consistent results.

This work describes the results of an investigation of the kinetics of indium electrodisolution and hydrogen evolution on indium in In(III)-free H<sub>2</sub>SO<sub>4</sub>.

## 2. Experimental

Indium electrodes (99.9999%) were cast under a nitrogen atmosphere into teflon-pyrex electrode holders and then stored under nitrogen until immersion in the electrolyte.

The 1 N sulfuric acid was prepared by diluting B and A reagent grade concentrated sulfuric acid with double distilled water. A solution of 1 N KOH was prepared by dissolving an appropriate quantity of reagent grade potassium hydroxide pellets in double distilled water. Solutions of different pH values were obtained by mixing quantities of the 1 N H<sub>2</sub>SO<sub>4</sub> and 1 N KOH until the desired pH was obtained. The reference electrode was a saturated calomel electrode.

Prepurified nitrogen was passed through a vycor tube containing a copper-silica catalyst which was heated to 300°C. The purified gas was then passed through two wash bottles and finally into the electrochemical cell to deaerate the electrolyte. During the experiments the cell was maintained at 27 ± 1°C.

After inserting the electrode into the cell, the

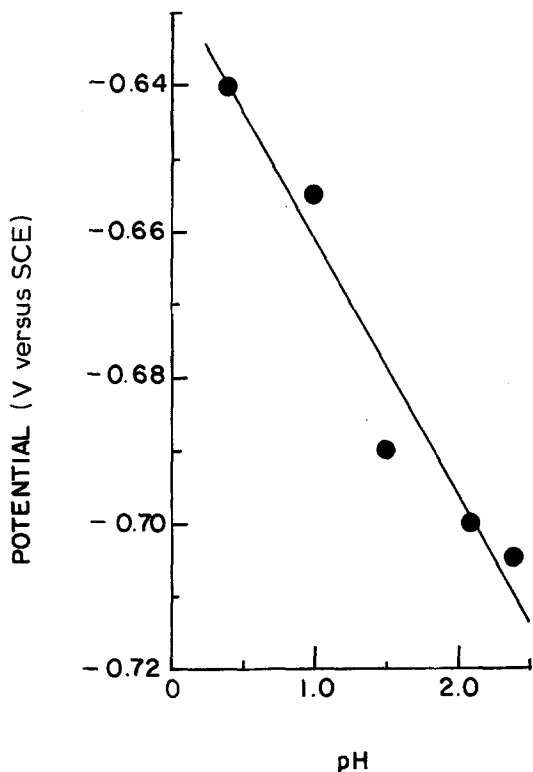


Fig. 1. Rest potential at various pH values.

rest potential was monitored for about 2 h. Then, the electrode was cathodically prepolarized to reduce the incipient indium oxide film and to remove the last traces of the dissolved oxygen in the solution. The cathodic polarization run was then initiated by increasing current steps. Polarization at each current step was maintained until a steady state potential was achieved. Steady state was usually observed within a time duration of about 5 min. After polarization at the largest current density was obtained, cathodic polarizations were continued in decreasing current steps until open circuit conditions were attained. These open circuit conditions were maintained for 2 h during which the rest potential was continuously monitored. Then, anodic polarization of the electrode was performed in increasing current steps. Steady state at each current step was usually achieved within 1 min. Deaeration was terminated during the anodic polarization runs since potential fluctuations were observed due to the bubbling of the deaerating nitrogen gas. However, this problem was not observed during cathodic polarization so

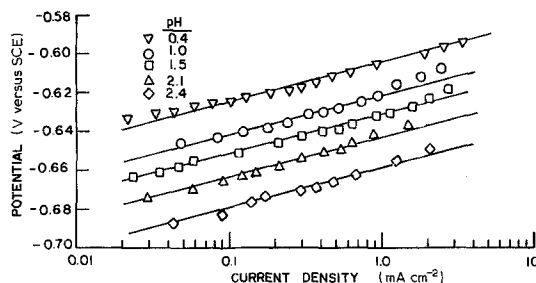


Fig. 2. The rate of anodic dissolution at various pH values.

that deaeration was continued throughout these experiments.

### 3. Results

The rest potentials of indium in different pH solutions of  $\text{H}_2\text{SO}_4$  are given in Fig. 1. The pH dependence of the rest potential of indium in  $\text{H}_2\text{SO}_4$  can be expressed as:

$$\frac{\partial \phi_m}{\partial \text{pH}} = -\frac{3}{5}(2 \cdot 303 RT/F). \quad (1)$$

The anodic dissolution behavior of indium in  $\text{H}_2\text{SO}_4$  is shown in Fig. 2. It is seen that hydroxyl ions accelerate the electrodisolution of indium in accord with the results of Losev and Molodov [5] for indium-amalgams in  $\text{HClO}_4$ . This phenomenon has also been reported for other metals in acidic sulfate solutions, such as iron [10] and nickel [11]. Fig. 2 shows that anodic Tafel slopes,

$$\left( \frac{\partial \phi}{\partial \log I_a} \right)_{\text{pH}} = 22 \pm 2 \text{ mV per decade} \quad (2)$$

provide a good fit of the experimental polarization data. The reaction order plot of Fig. 3 shows that the rate of electrodisolution is first order with respect to  $\text{OH}^-$ , that is,

$$\left( \frac{\partial \log i_a}{\partial \text{pH}} \right)_{\phi_a} = 1. \quad (3)$$

Losev and Molodov [5] obtained anodic Tafel slopes of 27 mV per decade and first order dependence with respect to  $\text{OH}^-$  for indium amalgams in  $\leq 0.2 \text{ M HClO}_4$  in accord with this work.

The cathodic polarization behavior of indium in  $\text{H}_2\text{SO}_4$  of various pH values is shown in Fig. 4. The results show that the rate of hydrogen evolution

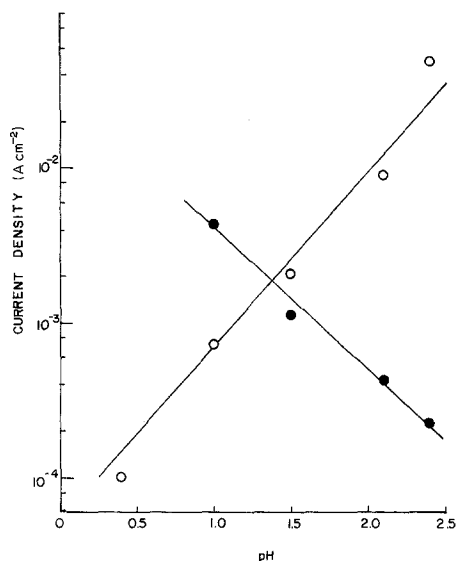


Fig. 3. Reaction order plots of anodic dissolution at  $-0.625$  V versus S.C.E. (open points) and hydrogen evolution at  $-1.2$  V versus S.C.E. (closed points).

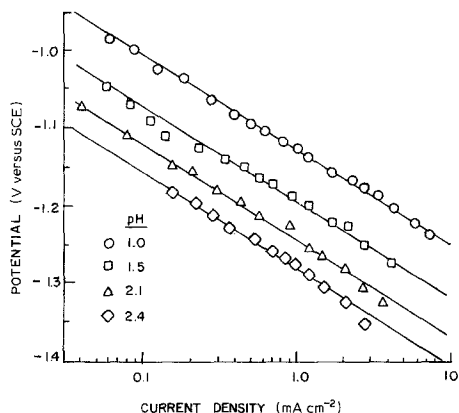


Fig. 4. The rate of hydrogen evolution at various pH values.

on indium increases as the H<sup>+</sup> concentration increases. A good fit of the experimental data is obtained with cathodic Tafel slopes

$$\left(\frac{\partial \phi}{\partial \log I_c}\right)_{[H^+]} = 120 \pm 5 \text{ mV per decade.} \quad (4)$$

The latter value has also been obtained by Butler and Dienst [9] for indium in 0.1 M HClO<sub>4</sub>. Fig. 3 shows first order dependence of hydrogen evolution with respect to H<sup>+</sup>, that is,

$$\left(\frac{\partial \log i_c}{\partial \log [H^+]}\right)_{\phi_c} = 1. \quad (5)$$

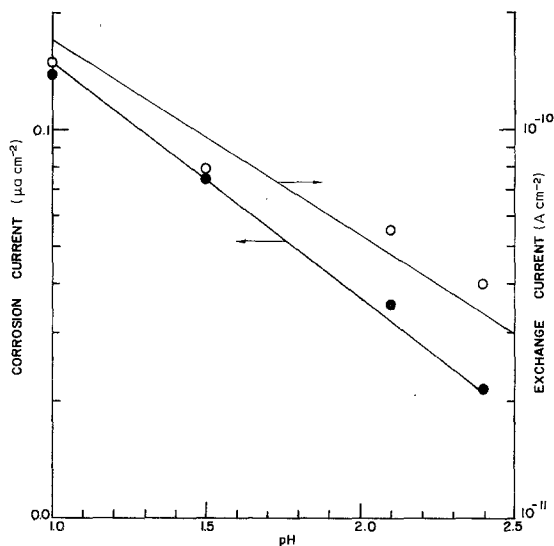


Fig. 5. Exchange current density for the hydrogen evolution reaction and the corrosion current density at various pH values.

The exchange current (for hydrogen evolution) dependence on pH,

$$\frac{\partial \log i_0}{\partial \text{pH}} = -0.5, \quad (6)$$

is shown in Fig. 5. The mixed currents (corrosion currents) are obtained by extrapolating the cathodic Tafel lines to the rest potentials. The pH dependence of the mixed current,

$$\frac{\partial \log i_m}{\partial \text{pH}} = -0.60 \quad (5)$$

is also shown in Fig. 5.

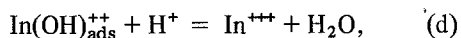
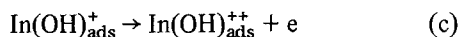
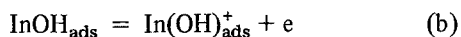
#### 4. Discussion

The Tafel slopes (120 mV per decade), reaction order (Equation 3) and exchange current densities (Equation 4 and Fig. 5) for the hydrogen evolution reaction on indium in H<sub>2</sub>SO<sub>4</sub> are consistent with the conclusions of Butler and Dienst [9] that hydrogen ion discharge is the rate determining step for hydrogen evolution on indium in 0.1 M HClO<sub>4</sub>. The rate of hydrogen evolution can be expressed as

$$I_c = k_c [H^+] e^{-\alpha F \phi / RT}. \quad (6)$$

The following mechanism will be shown to be consistent with the experimental results obtained

in this work for the electrodisso- lution of indium in  $H_2SO_4$ :



where Equation c is the rate determining step.

If  $\theta_{In(OH)}$ ,  $\theta_{In(OH)^+}$  and  $\theta_{In(OH)^{++}} \rightarrow 0$ , then Langmuir adsorption may be assumed. With Equation c as the rate determining step, Equations a and b are in quasi-equilibrium and the following expressions for  $\theta_{In(OH)}$  and  $\theta_{In(OH)^+}$  can be obtained:

$$\theta_{InOH} = \frac{k_{(a)}e^{F\phi/RT}}{k_{-(a)}[H^+]} \quad (7)$$

and

$$\theta_{InOH^+} = \frac{k_{(b)}k_{(a)}e^{2F\phi/RT}}{k_{-(b)}k_{-(a)}[H^+]} \quad (8)$$

where the symbols have their usual meanings. The rate of step (c) can be expressed as:

$$r_{(c)} = k_{(c)}(\theta_{In(OH)^+}) e^{(1-\beta)F\phi/RT}. \quad (9)$$

By substituting Equation 8 into Equation 9,

$$r_{(c)} = \frac{k_{(c)}k_{(b)}k_{(a)}e^{(3-\beta)F\phi/RT}}{k_{-(b)}k_{-(a)}[H^+]}. \quad (10)$$

Thus, the rate of anodic dissolution,  $I_a$ , is obtained.

$$I_a = k_a[OH^-]e^{(3-\beta)F\phi/RT}. \quad (11)$$

If the symmetry factors,  $\alpha = \beta = 0$ , Equations 6 and 11 become

$$I_c = k_c[H^+]e^{-F\phi/2RT} \quad (6a)$$

and

$$I_a = k_a[OH^-]e^{-5F\phi/2RT}. \quad (11a)$$

The pH dependence of the rest potential can be obtained by equating Equations 6a and 11a

$$\frac{\partial \phi_m}{\partial pH} = -\frac{2}{3} \left( 2.303 \frac{RT}{F} \right). \quad (12)$$

Both Equations 6a and 11a give the pH dependence of the mixed current since  $I_m = I_a = I_c$  at  $\phi = \phi_m$ , and thus,

$$\frac{\partial \log I_m}{\partial pH} = -\frac{2}{3}. \quad (13)$$

Table 1 compares the kinetic parameters

Table 1. Kinetic parameters for hydrogen evolution and electrodisso- lution of indium in  $H_2SO_4$  at 27°C

Kinetic parameters	Experimental	Theoretical
$\left( \frac{\partial \phi}{\partial \log I_a} \right)$ , mV per decade	$22 \pm 2$ mV	24
$\frac{\partial \log I_a}{\partial pH}$	+ 1	+ 1
$\frac{\partial \phi}{\partial \log I_c}$ , mV per decade	$120 \pm 5$	120
$\frac{\partial \log I_c}{\partial \log [H^+]}$	+ 1	+ 1
$\frac{\partial \log I_o}{\partial \log [H^+]}$	0.5	0.5
$\frac{\partial \phi_m}{\partial pH}$ , mV	- 36	- 40
$\frac{\partial \log I_m}{\partial pH}$	- 0.60	- 0.67

obtained experimentally and those calculated from the proposed mechanisms of hydrogen evolution and electrodisso- lution. It is seen that the mechanisms are in accord with the experimental results.

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