KINETICS OF THE PROCESSES LYING AT THE BASIS OF THE CORROSION OF IRON IN SULFURIC ACID SOLUTIONS

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The corrosion of iron in nonoxidative acid media is made up of the reactions of cathodic evolution of hydrogen and anodic ionization of the metal. A study of their kinetics is essential for an understanding of the nature of acid corrosion and the hydrogenation of the metal accompanying it.

METHOD OF INVESTIGATION

The polarization measurements were conducted by a galvanostatic method on a rotating disc electrode of Armco iron. The electrode represented a cylinder, pressed into a Teflon sleeve, which was fitted onto a rotating steel tube. The working end portion of the electrode was treated with fine polishing paper and degreased with ether, with alcohol, and electrochemically. The electrode, washed with double-distilled water and dried in a desiccator, was placed in the cell (Fig. 1). Solutions of sulfuric acid, $2 \cdot 10^{-4}$, $2 \cdot 10^{-3}$, $2 \cdot 10^{-2}$, $2 \cdot 10^{-1}$, 2 and 6 N, in which, in the case of acid concentrations $\leq 2 \cdot 10^{-1}$ N, sodium sulfate was introduced in the amount required to keep the total concentration of the electrolyte constant at 1.2 g-equiv/liter, were used as the electrolyte.

In the experiments we used double-distilled water, vacuum redistilled sulfuric acid [1], and twice recrystallized salts. The measurements were conducted in an atmosphere of purified electrolytic hydrogen.

Before the beginning of the experiments, air was displaced from the cell (Fig. 1) and reserve container with hydrogen. The electrolyte was introduced into the reserve container without breaking the

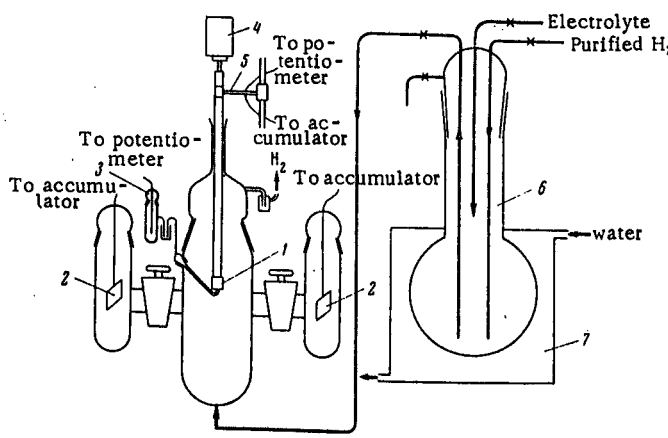

Fig. 1. Scheme of apparatus for recording polarization curves: 1) rotating disc electrode; 2) auxiliary platinum electrodes; 3) reference electrode; 4) motor; 5) sliding contact; 6) container for purifying solution from oxygen; 7) thermostat.

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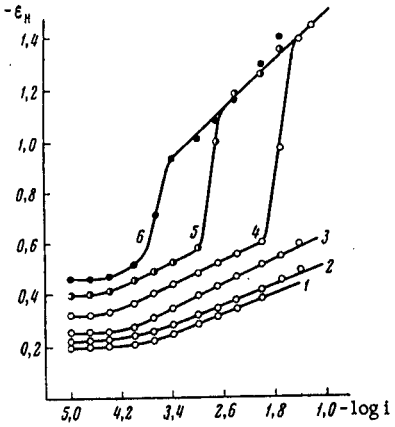

Fig. 2. Cathodic polarization curves of the evolution of hydrogen on iron in sulfuric acid solutions at various pH: 1) (−0.307); 2) 0.150; 3) 1.15; 4) 2.15; 5) 3.15; 6) 4.15.

hermetic seal, and there it was subjected to six alternate heatings to 60° and coolings to room temperature with continuous bubbling of hydrogen. The electrolyte, purified of the bulk of the oxygen and adjusted to the temperature of the experiment (18°), was forced over by hydrogen from the auxiliary container into the cell.

The measurements were conducted 30-40 min after immersion of the sample in the solution, when the stationary potential varied by no more than 1 mV in 5 min.

The test electrode was separated from the auxiliary platinum electrodes by ground joints, moistened with the working solution. A thin capillary led from the saturated calomel reference electrode to the rotating electrode. The distance from its tip to the surface of the electrode was determined with a cathetometer to consider the possible ohmic losses in the electrolyte. The ohmic losses in solution were usually extremely low, and the introduction of corrections was necessary only for the highest current densities.

All the elements of the apparatus, including the electrolyzer for the production of hydrogen and the system of its purification, were made of glass. If no stipulation is made, the disc electrode rotated at a rate of 1000 rpm. The potentials were converted to the hydrogen scale.

EXPERIMENTAL RESULTS

The cathodic polarization curves of iron in all the investigated solutions are shown in Fig. 2. At pH ≥ 2.15, limiting currents are detected on the curves, the magnitude of which decreases with increasing pH of the solution. After the limiting current plateau, all the experimental curves fit on approximately the same general straight line, independent of the pH of the initial solution.

The limiting current density (Fig. 3) varies with the number of revolutions m of the disc electrode, according to the equation

$$i_{lim} = \text{const}\sqrt{m}. \qquad (1)$$

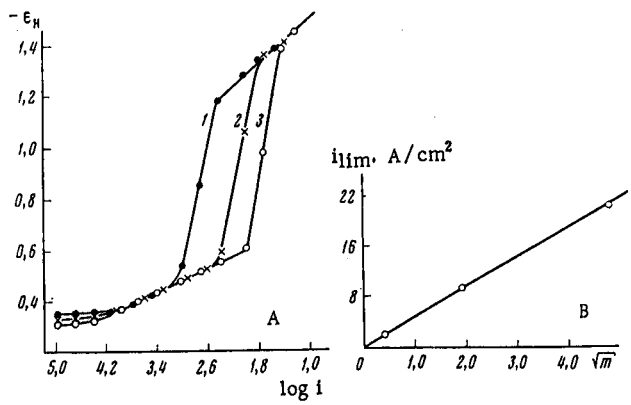

Fig. 3. Influence of the rate of rotation of the disc electrode on the diffusion current. A) Cathodic polarization curve in a solution of 1.2 g-equiv/liter ($H_2SO_4 + Na_2SO_4$) (pH 2.15) with various numbers of revolutions of the disc electrode per sec m; 1) 0.166, 2) 3.67, 3) 16.6; B) nature of the variation of the limiting diffusion current with the number of revolutions of the disc electrode.

The limiting current density is a linear function of the hydrogen ion concentration in solution

$$i_{lim} = k_{lim}[H^+]. \quad (2)$$

When the current density is expressed in $A \cdot cm^{-2}$ and the hydrogen ion concentration in $g\text{-equiv} \cdot cm^{-3}$, $k_{lim} = 1000$. Approximately the same value of the convective diffusion constant ($kT = 1100$) can be found according to the Levich formula [2] for a rotating disc electrode

$$k_T = 0.62z \cdot F \cdot \Delta^{2/3}\omega^{1/2}\nu^{-1/6}, \quad (3)$$

(when $\Delta = 2.6 \cdot 10^{-5}$ $cm^2 \cdot sec^{-1}$ [3] and $\omega = 104.2$ sec^{-1}).

All this permits us to conclude that the initial linear portions of the cathodic curves correspond to the reduction of hydroxonium ions, while the limiting portions are of a diffusion character. The upper portions of the curve evidently correspond to discharging of a water molecule [4-6].

The influence of pH on the stationary potential ε_c and the logarithm of the corrosion rate i_c is evident from Fig. 4. The anodic polarization curves are depicted in Fig. 5.

DISCUSSION OF THE EXPERIMENTAL RESULTS

In the self-dissolution of iron in acids, the rate of the reactions of cathodic deposition of the metal and anodic dissolution (ionization) of hydrogen can be neglected, and the corrosion rate i_c can be determined according to the point of intersection of the extrapolated linear portions of the cathodic and anodic polarization curves

$$i_K = i_a = i_c, \quad (4)$$

where i_K and i_a are the rates of evolution of hydrogen and ionization of iron, respectively, at the stationary potential ε_c.

The rate of evolution of hydrogen i_K in the region of the Tafel dependence can be found according to the equation

$$i_K = e^{\frac{2.3(\varepsilon_r - \varepsilon - a_k)}{b_K}} = e^{\frac{b_0 \ln [H^+]}{b_K} - \frac{2.3\varepsilon}{b_K} - \frac{2.3 a_k}{b_K}}, \quad (5)$$

where ε_r is the equilibrium potential of the hydrogen electrode in the given solution; $b_0 = 2.3\,RT/F$; a_k and b_K are the constants of the Tafel equation.

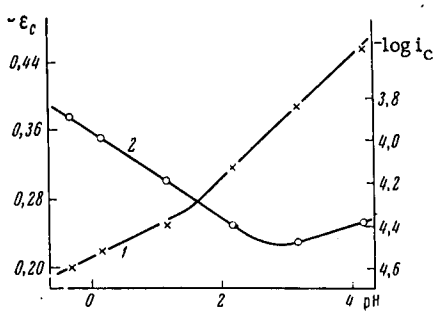

Fig. 4

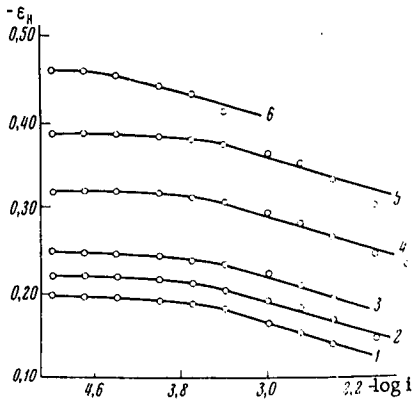

Fig. 5

Fig. 4. Dependence of the stationary potential (1) and corrosion rate (2) on the pH.

Fig. 5. Anodic polarization curves of iron in sulfate solutions with various pH: 1) (−0.307); 2) 0.150; 3) 1.15; 4) 2.15; 5) 3.15; 6) 4.15.

If the recombination of hydrogen atoms is decelerated in the case of evolution of hydrogen, then a_k does not depend upon the hydrogen ion concentration, and

$$i_K = k[H^+]^{b_0/b_K} e^{-2.3\varepsilon/b_K}. \qquad (6)$$

From Eq. (6) it is evident that the theory of decelerated recombination requires an order with respect to hydrogen ions equal to 0.5 ($b_0/b_K \approx 0.5$) for the cathodic reaction. Figure 6 shows that the reaction order calculated according to the cathodic polarization curve is close to the indicated value

$$\left[\left(\frac{\partial \log i_-}{\partial \log [H^+]}\right)_{\varepsilon=-0.39} = 0{,}6\right].$$

An analysis of the anodic polarization curves (Fig. 5) shows that at a constant potential, the rate of dissolution of iron depends upon the pH of the solution. A similar influence has been detected by a number of researchers [7-12], according to whose data the rate of anodic dissolution of iron is proportional to the OH^- concentration, either to the first [9] or to the second power [7, 8, 12].

In the sulfuric acid solutions that we investigated, two regions of pH with different values of the electrochemical order of the reaction with respect to hydroxyl ions ($\partial \log i_+ / \partial \log OH^-$) are detected. Up to pH $\approx$ 2, it is close to 1, while at higher pH it is close to 2 (Fig. 7).

In the region of pH < 2, the process of corrosion of the metal can be expressed on the basis of these data by the aggregate of the following reactions:

$$Fe + OH^- \rightleftarrows FeOH_{ad} + e \quad \text{rapid (a)}$$

or

$$\left.\begin{array}{l} FeOH_{ad} \rightleftarrows FeOH_{ad}^+ + e \\ FeOH_{ad} + H^+ + OH^- \rightleftarrows FeOH_{ad}^+ + H_2O + e \end{array}\right\} \quad \text{rate-determining (b),}$$

$$FeOH_{ad}^+ + nH_2O \rightleftarrows Fe^{2+} \cdot nH_2O + OH^- \quad \text{rapid (c).}$$

Then, according to this mechanism:

$$\left.\begin{array}{l} i_a = k_1'[FeOH_{ad}] \cdot e^{\beta F\varepsilon/RT} \\ \text{or} \\ i_a = k_1''[FeOH_{ad}][H^+][OH^-] \cdot e^{\beta F\varepsilon/RT}, \\ \text{where} \\ k_1' = k_1''[H^+][OH^-] = k_1'' k_w. \end{array}\right\} \qquad (7)$$

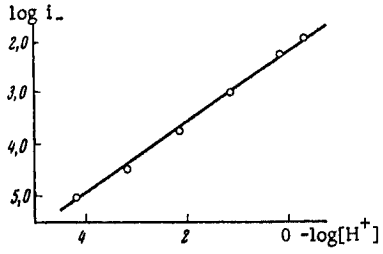

Fig. 6

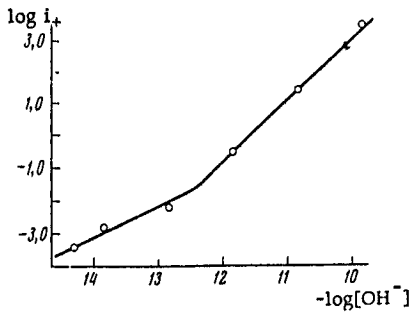

Fig. 7

Fig. 6. Order of the cathodic reaction of reduction of hydrogen at $\varepsilon = -0.39$ V with respect to hydrogen ions.

Fig. 7. Order of the reaction of dissolution of iron at $\varepsilon = -0.18$ V with respect to hydroxyl ions.

Assuming that step (a) is reversible, we can determine [$FeOH_{ad}$] according to the Nernst formula, and by substituting the expression for [$FeOH_{ad}$] into (7) we obtain:

$$i_a = k_1[OH^-]\exp\frac{(1+\beta)F\varepsilon}{RT}. \quad (8)$$

In the region of pH > 2

$$Fe + OH \rightleftarrows FeOH_{ad} + e \qquad \text{rapid (a)},$$

$$FeOH_{ad} + OH^- \rightarrow Fe(OH)_{2(ad)} + e \qquad \text{rate-determining (d)},$$

$$Fe(OH)_{2(ad)} + n\,H_2O \rightleftarrows Fe^{2+}\cdot n\,H_2O + 2OH^- \qquad \text{rapid (e)}.$$

From this

$$i_a = k_2'[FeOH_{ad}][OH^-]\cdot e^{\beta Fe/RT}. \quad (9)$$

Finding the value of [$FeOH_{ad}$] from Eq. (a), just as in the preceding case, and substituting it into (9), we obtain:

$$i_a = k_2[OH^-]^2\exp\frac{(1+\beta)F\varepsilon}{RT}. \quad (10)$$

Using the kinetic equations describing the cathodic (6) and anodic (8), (10) processes, we can derive expressions for the stationary potential and rate of corrosion as a function of the pH.

Thus, from (6) and (8) if follows that for the region of pH < 2:

$$k_1[OH^-]e^{2.3\varepsilon_c/b_a} = k[H^+]^{b_a/b_K}e^{-2.3\varepsilon_c/b_K} = k[H^+]^{0.5}e^{-2.3\varepsilon_c/b_K}. \quad (11)$$

Taking the logarithm and solving (11) with respect to ε_c, we arrive at

$$\varepsilon_c = \frac{b_K\cdot b_a}{b_K+b_a}\log\frac{k}{k_1k_w} - 1.5\frac{b_K\cdot b_a}{b_K+b_a}\,pH \quad (12)$$

or

$$\varepsilon_c = \varepsilon_c^0 - \vartheta_I pH. \quad (13)$$

Substituting the value of the stationary potential into the expression for i_k or i_a, we find an equation for the rate of corrosion at pH < 2:

$$\log i_c = \log k_1k_w + \frac{b_K}{b_a+b_K}\log\frac{k}{k_1\cdot k_w} + \left(1 - \frac{b_K}{b_K+b_a}\cdot 1.5\right)pH \quad (14)$$

or

$$\log i_c = \log i_c^0 + \gamma_I pH. \quad (15)$$

TABLE 1

pH <2	ϑ_{exp}	ϑ_I	ϑ_{II}	γ_{exp}	γ_I	γ_{II}
	0,040	0,043	0,059	—0,19	—0,12	0,5
pH >2	ϑ'_{exp}	ϑ'_I	ϑ'_{II}	γ'_{exp}	γ'_I	γ'_{II}
	0,075	0,074	0,088	+0,11	+0,14	0,25

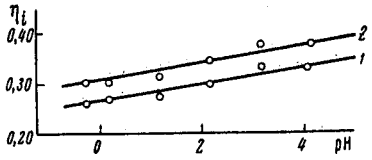

Fig. 8. Dependence of the hydrogen overvoltage on the pH at constant current density: 1) $4 \cdot 10^{-4}$ A/cm^2; 2) $1 \cdot 10^{-3}$ A/cm^2.

Using Eqs. (6) and (10), we can obtain analogous dependences for pH > 2:

$$\varepsilon_c = \frac{b_K \cdot b_a}{b_K + b_a} \log \frac{k}{k_2 \cdot k_w^2} - 2.5 \frac{b_K \cdot b_a}{b_K + b_a} \text{pH} \qquad (16)$$

or

$$\varepsilon_c = \varepsilon_c^{0'} - \vartheta_I' \text{pH}, \qquad (17)$$

$$\log i_c = \log k_2 \cdot k_w^2 + \frac{b_K}{b_K + b_a} \log \frac{k}{k_2 \cdot k_w^2} + \left(2 - 2.5 \frac{b_K}{b_K + b_a}\right) \text{pH} \qquad (18)$$

or

$$\log i_c = \log i_c^{0'} + \gamma_I' \text{pH}. \qquad (19)$$

The sharper influence of the pH upon the rate of ionization of iron and the stationary potential in the region of pH > 2 (Fig. 4) evidently is also related to the change in the mechanism of the ionization of iron (transition from first-order to second-order with respect to hydroxyl ions).

Table 1 compares the values of the coefficients at the pH from Eqs. (13), (15), (17), and (19), calculated under the condition of decelerated recombination of hydrogen atoms (ϑ_I, γ_I, ϑ_I' and γ_I') and the condition of decelerated discharging of hydrogen ions (ϑ_{II} and γ_{II})* with the experimental coefficients (ϑ_{exp} and γ_{exp}).

The corresponding equations for the cathodic evolution of hydrogen with an unchanged equation for the ionization of iron were used to calculate the coefficients (decelerated discharge).

The experimental data considerably better satisfy the values of the slopes ϑ and γ, calculated on the assumption of decelerated recombination. This is also indicated by the weak dependence of the hydrogen overvoltage upon the pH (Fig. 8) and the value of the reaction order with respect to hydrogen ions (Fig. 6), which, as it follows from the theory of decelerated recombination, is equal to 0.5.

Only the values of the slopes of the cathodic polarization curves, equal to 0.10-0.12, are in some contradiction with the conclusion of decelerated recombination. However, this is only an apparent contradiction, since for metals that absorb hydrogen well, the value of b_K cannot serve as a criterion of the mechanism of the hydrogen overvoltage.

In early studies devoted to the influence of pH on the rate of corrosion and the stationary potential [13-15], assumptions of independence of the rate of the anodic process from the pH of the solution were introduced. Such an assumption is justified in the presence of particles (for example, halide ions [12, 16, 17]) that prevent the catalytic action of OH^- ions. The slope of the anodic polarization curves is increased in this case, reaching 0.06 or more [12], which corresponds to direct transfer of metal ions to the solution.

In this work we considered a more general case, taking into consideration the possibility of the influence of the pH of the solution both on the cathodic and on the anodic processes.

CONCLUSIONS

1. In dilute solutions of sulfuric acid with addition of an indifferent electrolyte (sodium sulfate), the cathodic polarization curve on iron consists of two kinetic portions, separated by a region corresponding to the limiting diffusion current with respect to hydroxonium ions.

2. The kinetics of the liberation of hydrogen on the lower portion of the cathodic polarization curve is determined by recombination of hydrogen atoms, and on the upper portion more likely by discharging of water molecules.

* At pH < 2 $\vartheta_{II} = 2 \frac{b_K - b_a}{b_K + b_a}$ $\gamma_{II} = \left(1 - 2 \frac{b_K}{b_K + b_a}\right)$ At pH > 2 $\vartheta_{II}' = 3 \frac{b_K b_a}{b_K + b_a}$ $\gamma_{II}' = \left(2 - 3 \frac{b_K}{b_K + b_a}\right)$

3. In the region of pH < 2, the order of the reaction of anodic dissolution of iron with respect to hydroxyl ions is equal to 1, while at pH > 2, it becomes equal to 2.

4. The dependence of the stationary potential and rate of corrosion upon the pH, as well as experimental data on the influence of the pH of the solution upon the cathodic and anodic polarization curves in sulfuric acid solution, can be interpreted quantitatively with the assumption of deceleration of the recombination of hydrogen atoms and direct participation of hydroxonium ions in the process of anodic dissolution of iron.

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