MECHANISM OF THE ACCELERATING ACTION OF HYDROGEN SULFIDE ON THE DISCHARGE OF HYDROGEN IONS AT IRON

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Possible explanations for the stimulating effect of hydrogen sulfide on the rate of cathodic hydrogen evolution at iron are examined. The results from polarization and capacitance measurements at stationary and rotating disc electrodes are given. It is shown that the experimental data agree with the suggestion of a catalytic mechanism for the accelerating action of hydrogen sulfide on the discharge of hydrogen ions.

Hydrogen sulfide stimulates the corrosion of metals in the iron group by accelerating the cathodic and anodic reactions. The mechanism of the anodic reaction of the ionization of iron in acidic solutions in the presence of hydrogen sulfide was examined in [1, 2].

The cathodic and anodic polarization curves for iron of the Armco type (Fig. 1), recorded at 20°C in an atmosphere of hydrogen, show that in 0.1 N sulfuric acid solution the overpotential of the cathodic and anodic reactions decreases with increase in the hydrogen sulfide concentration, and the steady-state potential is shifted towards negative values on account of the greater acceleration of the anodic reaction.

The acceleration of the cathodic reaction by hydrogen sulfide was attributed to the formation of islets of FeS on the iron surface [3] or to the action of HS^- ions, during adsorption of which a ψ_1 potential with negative sign appears [4]. Phase films of iron sulfides are in fact formed on iron and play a major part in its hydrogen sulfide corrosion at pH values above 4 [5, 6]. It is, however, completely absent in more acidic solutions (at pH values below 3), as follows from differential capacitance data and from the equilibrium diagram. As far as the supposed action of the ψ_1 potential during adsorption of HS^- ions is concerned, they (like halide ions) are tightly bound by the surface iron atoms, but HS^- anions accelerate and halide anions retard the cathodic hydrogen ion discharge reaction.

There is one other contradiction. The adsorption, determined by means of labeled sulfur atoms, decreases with increase in the negative potential [7], and this favors adsorption not of hydrogen sulfide molecules but of HS^- ions. However, the decrease in the differential capacitance with increase in the negative potential (Fig. 2) indicates an increase in the adsorption.*

From Fig. 1 it is seen that the higher the hydrogen sulfide concentration the stronger the accelerating action of the negative potential on the cathodic evolution of hydrogen, although the adsorption of HS^- ions should decrease with increase in the negative potential.

*From Fig. 2 it is seen that the capacitance curve is lower with small hydrogen sulfide concentrations (10^{-5} N) and higher with larger concentrations than the capacitance curve for a pure solution of 0.1 N sulfuric acid. The same applies to 1.0 and 0.01 N sulfuric acid. This can be explained by the fact that the first portions of HS^- are adsorbed on active parts of the electrode, being firmly attached to it, and reduce the capacitance, as in the case of halide ions on iron and nickel [9]. At higher hydrogen sulfide concentrations the HS^- ions are adsorbed on less active parts of the surface, and the capacitance increases, as in the case of the adsorption of anions on mercury.

M. V. Lomonosov Moscow State University. Translated from Zashchita Metallov, Vol. 10, No. 1, pp. 17-21, January-February, 1974. Original article submitted June 28, 1972.

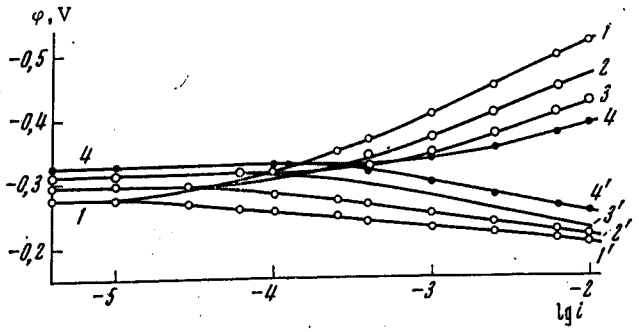

Fig. 1. Cathodic and anodic polarization curves for an iron electrode in 0.1 N sulfuric acid (1) with addition of hydrogen sulfide: 2) 10^{-6}; 3) 10^{-4}; 4) 10^{-2} N.

It has been suggested [8] that the acceleration of the cathodic hydrogen evolution is achieved as a result of easier reduction of adsorbed H_3S^+ particles obtained by the protonation of adsorbed H_2S molecules by H_3O^+ ions. However, this idea contradicts the above-mentioned experiments [7]. Another similar scheme of facilitated discharge of hydrogen from H_2S molecules has been proposed [10, 11]: $H_2S + e \rightarrow 1/2H_2 + HS_1^-$; $HS^- + H_3O \rightarrow H_2S + H_2O$. It was based on the fact that a region of limiting current was observed, on the curves for the dependence of the current strength on the potential of an iron electrode, recorded during the passage of a mixture of $H_2S + N_2$ gases through a sodium chloride solution, and its density increased with increase in the partial pressure of hydrogen sulfide in the gas mixture. In these experiments, however, the pH was not constant, and the dependence of I_{lim} on the partial pressure of hydrogen sulfide did not obey the laws of diffusion kinetics.

In the experiments which we carried out with a rotating iron disc electrode in 0.1 and 1.0 N sulfuric acid solutions with hydrogen sulfide additions no areas of limiting current were observed on the I, φ curves in the region of current densities calculated in accordance with the Levich equation. In less acidic solutions (0.5 N KCl + H_2S at pH 2 or 4) the I, φ curves had clearly defined areas of limiting current, but they were not due to the presence of hydrogen sulfide in the solution, since the I_{lim} value remained unchanged when the hydrogen sulfide concentration was changed from zero to 10^{-2} N (Fig. 3). With constant hydrogen sulfide concentration the limiting current decreased in proportion to the decrease in the concentration of acid in the solution. These experiments show that the limiting current areas are due only to concentration polarization in hydrogen ions and that hydrogen sulfide is not directly required in the cathodic reaction, but its presence in the solution accelerates the discharge of hydrogen ions.

From Fig. 3 it can be seen that hydrogen sulfide accelerates the cathodic reaction with currents below I_{lim}, where the solution at the electrode surface is acidic. With currents greater than I_{lim} the solution at the electrode surface becomes alkali, hydrogen is released from the water molecules, and the presence of hydrogen sulfide leads to the opposite effect, i.e., an increase in the overpotential and retardation of this reaction. This agrees with the retarded discharge theory.

A catalytic mechanism of hydrogen evolution, similar to that which was formulated by Le Boucher [7] on the basis of measurement of the adsorption of HS^- anions and investigation of the diffusion rate of hydrogen through iron plates, is likely. This can be expressed in terms of the following scheme:

$$Fe + HS^- = Fe(HS^-)_a, \quad (a)$$

$$Fe(HS^-)_a + H_3O^+ = Fe(H-S-H)_a + H_2O, \quad (b)$$

$$Fe(H-S-H)_a + e \rightarrow Fe(HS^-)_a + H_a, \quad (c)$$

$$\downarrow$$

$$H^+ \text{ — Diffusion into metal.}$$

Stages (a) and (b) are quasireversible and take place more rapidly than stage (c), which determines the rate of the whole process:

$$i = k[Fe(H-S-H)_a]\exp -[\alpha(\varphi - \psi_1) - \psi_1]F/RT, \quad (d)$$

$$i = k[HS^-][H_3O^+]\exp -[\alpha(\varphi - \psi_1) - \psi_1]F/RT,$$

$$\varphi = a - \psi_1 \frac{1-\alpha}{\alpha} + \frac{RT}{\alpha F}\{\ln[H_3O^+] + \ln[HS^-] - \ln i_k\}. \quad (e)$$

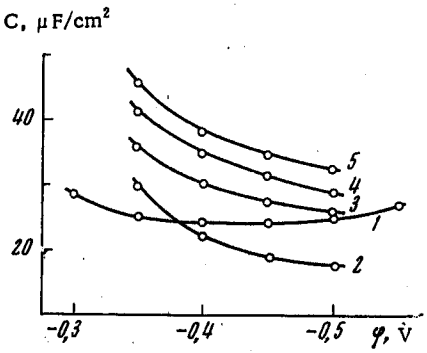

Fig. 2

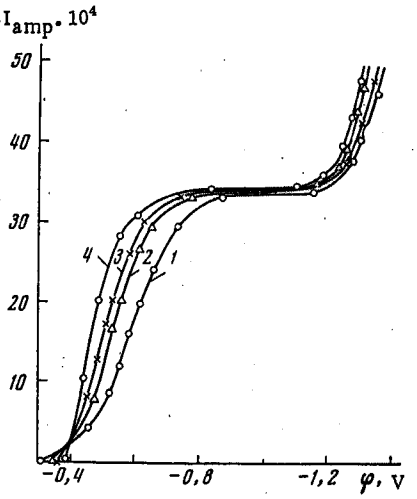

Fig. 3

Fig. 2. Differential capacitance curves for zone-melted iron in 0.1 N sulfuric acid (1) with additions of hydrogen sulfide: 2) 10^{-5}; 3) 10^{-4}; 4) 10^{-3}; 5) 10^{-2} N.

Fig. 3. Cathodic polarization curves for rotating iron disc electrode in 0.5 N potassium chloride solution at pH ≈ 2 (1) and with additions of hydrogen sulfide: 2) 10^{-4}; 3) 10^{-3}; 4) 10^{-2} N. Rotation rate 460 rpm.

Substituting the concentration of the catalyst from Eq. (b) in Eq. (d), we obtain Eq. (e), in which (as follows from the experiment) with constant pH and ψ_1 the concentration $(HS^-)_a$ is a function of the potential and hydrogen sulfide concentration in the solution.

The HS^- ions, adsorbed on the iron surface through chemical and electrochemical forces, add protons from the hydrogen ions of the solution and form a molecular catalyst complex $Fe(H-S-H)_a$. During cathodic polarization the protons of this catalyst are reduced to hydrogen atoms with subsequent recombination to molecules or diffuse into the metal, without reduction, giving rise to hydrogen embrittlement. As a result of these reactions adsorbed HS^- ions are regenerated on the iron. The surface concentration and the strength of the bond between the HS^- anions and the iron atoms decrease with increase in negative potential, but the concentration and activity of the catalyst increase, since the hydrogen ions are capable of coming closer to the electrode and the protons add more readily to the adsorbed HS^- anions. At more positive potentials the strength of the bond between the HS^- ions and the metal becomes so great that the labile complex is not formed and the cathodic catalytic effect is not realized. This probably explains the disappearance of the accelerating action of hydrogen sulfide observed on the cathodic polarization curves with small currents and the retardation of the cathodic reaction (Figs. 1 and 3). This shows that as the strength of the bond between the HS^- anions and the ion increases they begin to behave like halide ions.

Our results can be easily explained from this standpoint, and this can serve as confirmation of the proposed mechanism. The experiments with the rotating iron disc electrode, which showed that hydrogen sulfide is not discharged directly in the cathodic reaction but accelerates the hydrogen ion discharge reaction, indicate a catalytic mechanism for this reaction. The decrease in the slope of the Tafel lines with increase in the hydrogen sulfide concentration (Fig. 1) evidently occurs as a result of increase in the surface concentration and activity of the catalyst. The decrease in the adsorption of HS^- anions with displacement of the potential towards the negative side, determined by means of the radioactive sulfur isotope, results from the action of electrostatic forces. The decrease in the differential capacitance with increase in negative potential (Fig. 2), which indicates an increase in the adsorption, evidently takes place as a result of the fact that the capacitance changes not only on account of adsorption of HS^- anions but also on account of adsorption of the catalytic molecular complex. As indicated above, the surface concentration of this catalyst increases with increase in negative potential. Consequently, the above-mentioned effect can be explained if it is assumed that the decrease in capacitance through increase in the catalyst concentration

predominates over its increase on account of decrease in the surface concentration of HS^- anions. *

In the light of the theory presented above it is possible to explain the prevention of the stimulating action of hydrogen sulfide with the addition of an inhibitor, the increase in its adsorption, and the observed synergistic effect during the occurrence of the cathodic reaction. By acting as anionic bridges, the HS^- ions adsorbed on the iron promote adsorption of inhibitors of cationic types (R^+). Here the latter fill the adsorption bond in the $Fe(HS^-)$ to form a fairly stable surface molecular compound Fe(H–S–R), which is incapable of transferring protons from the solution to the electrode. In addition, the adsorbed cations of the inhibitor shift the adsorption ψ_1 potential towards the positive side, and this is the reason for retardation of the cathodic hydrogen ion discharge reaction.

LITERATURE CITED

1. Z. A. Iofa, Zashchita Metallov, 6, 491 (1970).
2. Z. A. Iofa and Vei Bao Min, Catalytic Reactions in the Liquid Phase [in Russian], Alma-Ata (1963), p. 200.
3. V. A. Karnitskii and N. A. Golubev, Zh. Prikl. Khim., 8, 864 (1935).
4. V. A. Kuznetsov and Z. A. Iofa, Zh. Fiz. Khim., 31, 201 (1947).
5. S. Sardisco and R. Pitts, Corrosion, 21, 245 (1965).
6. R. Hausler, L. Goeller, and R. Rosenwald, 3 Europ. Sympos. on Corros. Inhibit. Ferrara (1970), p. 331.
7. B. Le Boucher, Rev. Franc. du Petrole, 18, No. 4, 1-66 (1963); Extended Abstracts the 4th Intern. Congress on Metall. Corros. Amsterdam (1969), p. 145.
8. V. F. Panasenko, Candidate's Thesis [in Russian], Kievsk. Polit. Inst. (1972).
9. E. I. Mikhailova and Z. A. Iofa, Élektrokhimiya, 6, 231 (1970).
10. P. Bolmer, Corrosion, 21, 69 (1965).
11. H. Kaesche, Werkstoffe und Korrosion, 3, 185 (1970).

*This conclusion can be reached during comparison of the values for the adsorption of HS^- anions (Γ_{HS^-}) and the number of protons (V_{H^+}) discharged in 1 sec on 1 cm^2 of surface as a function of the potential, according to data from [7], for a solution containing 6.7 mM H_2S + 10 mM NaCl, pH ~ 4

φ(V) —	0,80	—0,90	—1,00	—1,10	—1,20	—1,40
$\Gamma_{HS^-} \cdot 10^{15}$	4,5	3,4	3,0	2,6	2,2	1,4
$V_{H^+} \cdot 10^{15}$	0,26	0,69	1,75	4,0	5,0	3,56
V_{H^+}/Γ_{HS^-}	0,07	0,21	0,58	1,56	2,26	2,64

The increase in the mean activity of the catalyst (V_{H^+}/Γ_{HS^-}) with increase in negative potential must be assumed to be due to increase in its surface concentration.