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Abstract

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ADSORPTION OF SULFUR ON IRON FROM ACID SOLUTIONS OF HYDROGEN SULFIDE

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In connection with the study of the mechanism of processes associated with the stimulating and inhibiting action of hydrogen sulfide on the corrosion of iron in acid solutions in the presence of certain organic compounds (^{1}), it was of interest to measure the adsorption of sulfur on iron from these solutions.

Adsorption was measured using the method of radioactive isotopes. From radioactive sulfur (S^{35}) and iron powder, ferrous sulfide was prepared; it was decomposed with a solution of H_2SO_4, and the radioactive hydrogen sulfide evolved, while hydrogen was passed through, was transferred into $0.1\,N$ NaOH. A 0.05—$0.7\,N$ Na_2S^* solution was obtained. Plates of chemically pure iron (Hilger) or Armco iron, after degreasing, were placed for a definite period in a solution of $H_2SO_4 + Na_2S^*$, removed, washed with distilled water, and dried. The experiment showed that complete removal of excess solution occurs after 3 minutes of washing; in all cases we washed for 5 minutes. The radioactivity of the plates was determined with an end-window counting tube. The specific activity of the solutions was measured from the number of pulses from a small drop, weighed on an analytical balance, of the alkaline solution diluted with water, deposited on a silver or copper plate and dried to complete dryness over an electric hot plate. The roughness factor of the plates was estimated by comparing the number of pulses after sulfur adsorption under identical conditions, given by the given plate and by a well-polished plate; for the latter it was taken as equal to 1.2.

Table 1

Adsorption from a solution of $0.1N$ H_2SO_4+

Concentration Na_2S, N	Adsorption duration, min	Γ, $(\text{g-equiv/cm}^2)10^{10}$
$1.5 \cdot 10^{-5}$	3	10
$1.5 \cdot 10^{-5}$	15	32
$1.5 \cdot 10^{-5}$	30	36
$1.5 \cdot 10^{-4}$	1	20
$1.5 \cdot 10^{-4}$	3	36

Concentration Na_2S, N	Adsorption duration, min	Γ, (g-equiv/cm^2)10^{10}
$1.5 \cdot 10^{-4}$	15	44
$1.5 \cdot 10^{-3}$	1	33
$1.5 \cdot 10^{-3}$	5	43
$1.5 \cdot 10^{-3}$	150	110

Table 1 gives the mean results of measurements of adsorption on chemically pure iron, in g-equiv per 1 cm^2 of true surface, at $t = 20°$. Experiments with Armco iron gave an analogous result.

Addition of the inhibitor $N(C_4H_9)_4{}^+$ did not change the magnitude of adsorption (see Table 2).

Table 2

Concentration, N	Concentration, N	Concentration, N	Adsorption duration, min	Γ, (g-equiv/cm^2)10^{10}
Na_2S	H_2SO_4	$N(C_4H_9)_4{}^+$		
$1.5 \cdot 10^{-5}$	0.1	no	15	40
$1.0 \cdot 10^{-3}$	1.0	$1.4 \cdot 10^{-3}$	1	32
$1.0 \cdot 10^{-3}$	1.0	$1.4 \cdot 10^{-3}$	15	45
$1.5 \cdot 10^{-3}$	0.1	10^{-3}	5	43
$1.5 \cdot 10^{-3}$	1.4	10^{-3}	5	42
$1.5 \cdot 10^{-3}$	6.0	10^{-3}	5	38

The increase in adsorption with time in the case of an acid solution containing more than $10^{-4} N$ Na_2S without inhibitor is evidently connected with an increase of the surface as a result of etching. The surface of the plate, moreover,

already after 6-10 minutes becomes covered with blisters of swelling, the number and size of which increase with the etching time. In the presence of an inhibitor the plates remain smooth and shiny; adsorption increases little with time.

The increase in the measured value of adsorption during prolonged residence of the plate in the solution may also be caused by radiation from sulfur that has penetrated into the depth of the metal. This penetration was determined by measuring the radioactivity of iron plates after adsorption from a solution of $1N$ $H_2SO_4 + 4.6 \cdot 10^{-4} N$ Na_2S^*, successive removal of the upper layer of metal with fine emery paper (No. 000), and weighing on an analytical balance. Penetration of the anions SO_4^{2-}, as well as J^- and Br^-, into the depth of the plate had previously been found by N. A. Balashova (^{3}).

[Figure 1: ordinate I, cpm; abscissa "Thickness of the removed layer," μ.]

Figure 1 shows the curve of the change in activity of the plate as the layer of metal is removed from the surface; it is evident from it that some amount of sulfur (about 10%) penetrates into the depth of the metal by more than 1.5μ.* The absorption of electrons emitted by S^{35} by a 1μ layer of iron does not exceed 10–12% (found from the absorption curve for layers of aluminum foil, assuming the same absorption per 1 mg/cm^2 for Al and Fe).

As is evident from the data of Table 3, the experiments showed that the rate of dissolution of iron in a sulfuric-acid solution containing H_2S is almost unchanged by the addition of KJ; however, this rate increases greatly if Na_2S is added to the solution $H_2SO_4 + KJ$.

It may be concluded that adsorbed sulfur is bound to iron more strongly than iodine, and that the latter is displaced from the surface during adsorption of sulfur, since the retarding action of KJ almost completely disappears when Na_2S is added to the solution (Table 3, rows 3 and 4), whereas the addition of KJ to the solution $H_2SO_4 + Na_2S$ practically does not change the amount of sulfur adsorption (Table 4).

Table 3

Rate of dissolution of iron in $1N$ H_2SO_4+

Na_2S	KJ	$N(C_4H_9)_4^+$	Dissolution rate, g/cm$^2 \cdot$ h
no	no	no	$4 \cdot 10^{-4}$
0.001	no	no	$9 \cdot 10^{-4}$
0.001	0.001	no	$7.8 \cdot 10^{-4}$
no	0.001	no	$2.2 \cdot 10^{-5}$
0.001	0.001	0.001	$7.2 \cdot 10^{-6}$
0.001	no	0.001	$1.2 \cdot 10^{-5}$

However, the strongly pronounced corrosion-retarding action of the ions $N(C_4H_9)_4^+$ in a solution containing Na_2S and KJ, compared with the action of an acid solution containing only Na_2S (Table 3, rows 5 and 6), indicates the presence on the surface

Table 4

H_2SO_4	Na_2S	KJ	$N(C_4H_9)_4^+$	Duration of adsorption, min	Γ, (g-equiv/cm^2)$\cdot 10^{10}$
1.0	$1.2 \cdot 10^{-3}$	no	no	5	44
0.1	$1.2 \cdot 10^{-3}$	$0.5 \cdot 10^{-3}$	no	5	42
1.0	10^{-3}	$0.5 \cdot 10^{-3}$	$1.4 \cdot 10^{-3}$	20	46
1.0	10^{-3}	no	10^{-3}	20	45

* The slight initial delay on the radioactivity-decay curve when very thin metal layers are removed is evidently connected with the fact that the grain size of the emery-paper abrasive is 0.2—0.3μ.

significant amounts of iodine (1, 2). Indeed, experiments on measuring the adsorption of iodine ions on iron from solutions of H_2SO_4 + KI using labeled KI^{131} showed that in the presence of Na_2S the adsorption of iodine decreases by only 20-25%.

Experiments in recording polarization curves indicate a decrease in the hydrogen overvoltage on iron when Na_2S is added to an H_2SO_4 solution. However, the presence in the acid solution of an organic inhibitor, for example tetrabutylammonium sulfate, simultaneously with Na_2S leads to a considerable increase in the overvoltage.

It should also be noted that the addition of an inhibitor to a solution of H_2SO_4 + H_2S prevents the appearance of hydrogen embrittlement during the etching of iron in it. Thus, for example, a steel wire 0.2 mm thick, cathodically polarized by a current of 0.01 A/cm^2 under a load of 1 kg in a solution of 1 N H_2SO_4 + 10^{-3} N Na_2S, breaks after 2-3 min; however, after the addition of 10^{-3} mole/liter of tetrabutylammonium sulfate it does not break for 4-5 hours. In pure 1.0 N H_2SO_4 the wire likewise does not break for 4-5 hours.

The adsorption of sulfur on iron is an irreversible process. This follows from the fact that it is almost unchanged by prolonged washing of the plate with water. When the plate was washed with a 1 N H_2SO_4 solution for 10 min, the adsorption decreased only from $35 \cdot 10^{-10}$ to $27 \cdot 10^{-10}$ g-equiv/cm^2.

The average value of sulfur adsorption over 5 min from a solution of 1 N H_2SO_4 + 0.001 N Na_2S is $42 \cdot 10^{-10}$ g-equiv/cm^2, or $21 \cdot 10^{-10}$ g-atoms of sulfur per 1 cm^2. This value is somewhat smaller than that required for the formation of a diatomic layer of S^{2-} ions ($r = 1.84$ Å; for a monolayer $\Gamma = 12.3 \cdot 10^{-10}$ g-equiv/cm^2). The indicated adsorption value corresponds to the bonding of slightly less than one sulfur atom with one iron atom (for α—Fe, $r = 1.238$ Å; on the surface, $27 \cdot 10^{-10}$ g-at/cm^2). However, an exact calculation of the adsorption value cannot be made because of the penetration of sulfur into the depth of the metal.

Comparison of the above data with the value of iodine adsorption on iron (4) nevertheless shows that sulfur covers a considerably larger part of the iron surface.

The stimulating action of hydrogen sulfide on the rate of dissolution of iron in acids, associated mainly with acceleration of the anodic process (5), is apparently caused by a weakening of the bond between iron atoms and by facilitation of their ionization owing to the formation of a strong bond between iron atoms and sulfur.*

It is also necessary to explain the disappearance of the stimulating action of hydrogen sulfide in the presence of certain inhibitors and the enhancement of their retarding action on corrosion in the presence of H_2S compared with the action of these inhibitors in the absence of the latter. Experiments showed that, at a given inhibitor concentration in the solution, there is an optimum H_2S concentration at which the maximum retarding effect is observed. Increasing the concentration of the inhibitor, for example tribenzylamine, makes it possible to increase the H_2S concentration to 10^{-2} N without lowering the combined corrosion-retarding effect.

It is important to note that H_2S substantially enhances the inhibiting action only in the case of organic bases; organic acids and alcohols, for example caproic acid or hexyl alcohol, as well as sulfo acids, increase the stimulating action of H_2S.

These facts make it possible to suggest that the cations of the inhibitor form firmly bound pairs (by electrostatic forces) with the Fe–S dipoles formed on the iron surface. The number of these pairs per unit surface is determined by the concentration of the inhibitor in the solution. When the inhibitor concentration is insufficient, the stimulating properties of H_2S are retained. This may be confirmed by the above-mentioned increase in hydrogen overvoltage in the acid solution in the joint presence of H_2S and the inhibitor, and the associated decrease in the rate of dissolution of iron. At the same time, there is probably a decrease in the surface concentration of adsorbed hydrogen atoms $[H]_s$, as indicated by the decrease in hydrogen embrittlement at $i = \text{const}$ in an $H_2SO_4 + H_2S$ solution upon addition of an organic base. As in the case of the joint action of halide ions and organic bases in the presence of As_2O_3 (^{7}), the decrease in embrittlement, associated with a decrease in the rate of diffusion of atomic hydrogen into the metal, is caused by an increase in the cathodic potential due to the addition of inhibitors and by an increase in the rate of removal of hydrogen by the electrochemical mechanism.

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* A somewhat different mechanism for the stimulating action of hydrogen sulfide was proposed by Makrides and Hackerman (6).

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