INFLUENCE OF HYDROGEN SULFIDE, INHIBITOR, AND pH OF THE MEDIUM ON THE RATE OF ELECTROCHEMICAL REACTIONS AND THE CORROSION OF IRON

Z. A. Iofa and Fan Lyong Kam

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This communication presents data on the influence of pH, hydrogen sulfide, and an inhibitor on the electrochemical reactions and corrosion of iron in deaerated solutions of H_2SO_4, with concentrations from 0.01 to 8.0 N at 20° (at H_2SO_4 concentrations less than 1 N, Na_2SO_4 was added up to 1N). The electrode was zone melted iron and Armco type iron; the pH was measured with a hydrogen electrode in the cell itself, and with a glass electrode outside the cell. Tribenzylamine (TBzA) was used as a standard cationic type inhibitor. Instead of H_2S, the salt $Na_2S \cdot 9H_2O$ was added to the solutions, assuming that it is almost entirely converted to H_2S in acid solutions.

From Fig. 1 it is evident that for zone-melted iron the potential of the cathodic reaction of discharging of hydrogen ions (φ_c) is shifted in the positive direction with increasing hydrogen sulfide concentration, while the potential of the anodic reaction of ionization of iron (φ_a) is shifted in the negative direction. Consequently, hydrogen sulfide accelerates both reactions. The static corrosion potential φ_{corr} is shifted in the negative direction with increasing hydrogen sulfide concentration as a result of the stronger acceleration of the anodic reaction, while the current of self-dissolution (i_s) increases. The corresponding coefficients are cited below.

$\partial\varphi_c/\partial p_{Na_2S} = -19$ mV at $i_c = 10^{-3}$ A/cm^2, $\partial\varphi_a/\partial p_{Na_2S} = 22.5$ mV at $i_a = 10^{-3}$ A/cm^2, $\partial\varphi_{corr}/\partial p_{Na_2S} = 13$ mV$-\partial \log i_c/\partial p_{Na_2S} = -0.15$ at $\varphi_c = -0.35$ V, $\partial \log i_a/\partial p_{Na_2S} = -0.40$ at $\varphi_a = -0.25$ V, $\partial \log i_{corr}/\partial p_{Na_2S} = -0.21 - p_{Na_2S} = -\log [Na_2S]$.

A comparison of the curves of Figs 2a and 3a shows that the accelerating effect of hydrogen sulfide on the cathodic reaction is stronger in less acid solutions, and on the anodic reaction in more acid solutions. The decelerating action of the inhibitor, together with hydrogen sulfide, on the cathodic reaction, on the contrary, is manifested more strongly in more acid solutions, and on the anodic reaction in less acid solutions (see also Fig. 2b).

TABLE 1

Derivatives of parameters of the process and pH	Without additives	$+Na_2S$ $\cdot 10^{-4}$N	$+10^{-4}Na_2S$ $+10^{-4}$ M TBzA
$\partial\varphi_c/\partial$pH	−82mV	−73mV	−62mV
$\partial\varphi_a/\partial$pH	−35mV	−43mV	−41mV
$\partial \lg i_c/\partial$pH	−0,80	−0,72	−0,65
$\partial \lg i_a/\partial$pH	+0,85	+0,92	—
$\partial \lg i_{corr}/\partial$pH	−0,28	−0,31	+0,08

TABLE 2. Rate of Corrosion of Iron, $i_{corr} \cdot 10^4$ A/cm^2

Additive	Concentration of H_2SO_4, N		
	0,1	3,0	8,0
None	1,0	2,7	4,96
10^{-4} N Na_2S	2,5	5,64	8,0
10^{-4} N Na_2S + $+ 10^{-4}$ M TBzA	0,013	0,083	0,12

M. V. Lomonosov Moscow State University. Translated from Zashchita Metallov, Vol. 10, No. 3, pp. 300-303, May-June, 1974. Original article submitted November 14, 1972.

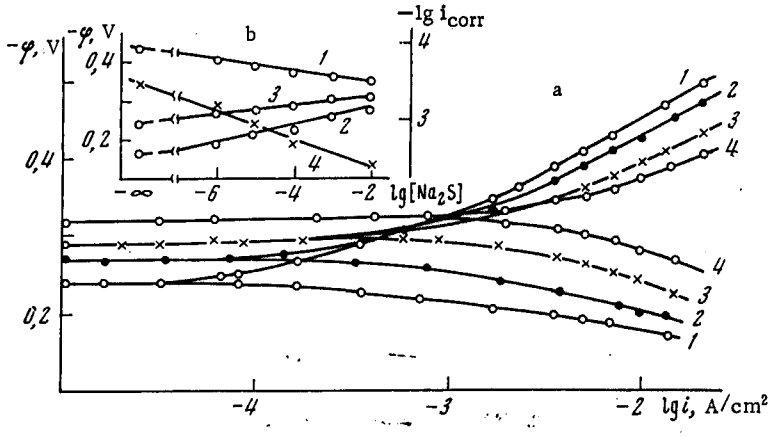

Fig. 1. Cathodic and anodic polarization curves of zone-melted iron (a) in 1 N H_2SO_4 (1) and with additions of Na_2S (N): 2) 10^{-6}; 3) 10^{-4}; 4) 10^{-2}, as well as dependence of the electrode potential on the logarithm of the Na_2S concentration in 1 N H_2SO_4 (b): 1) φ_c; 2) φ_a at 10^{-2} A/cm^2; 3) φ_{corr}; 4) dependence of log i_{corr} on log [Na_2S].

The rate of the cathodic reaction decreases, and that of the anodic reaction increases with increasing pH (Fig. 3b). The rate of self-dissolution of iron is a compromise between the rates of the individual electrochemical reactions; therefore, the dependence of log i_{corr} on the pH is less pronounced than the corresponding dependence of the individual electrochemical reactions (Table 1).

In solutions with hydrogen sulfide and without it, the rate of self-dissolution of iron decreases with increasing pH, while in the presence of additions of TBzA + Na_2S it increases somewhat (Table 1). The acceleration of the corrosion of hydrogen sulfide at all values of the pH is almost the same while the deceleration of the corrosion on the addition of TBzA + Na_2S decreases substantially with increasing pH (curves of log i_{corr} versus the pH for solutions with and without the inhibitor approach one another with increasing pH). The latter effect is associated with the lower adsorbability of the inhibitor with increasing pH of the solution, which probably occurs as a result of the competitive adsorption of OH^- ions, just as in the case of the adsorption of inhibitors on iron in the absence of hydrogen sulfide [1].

The rate of corrosion of iron, determined according to the weight loss of the samples, is very close to that found from the polarization curves; however, in the case of an addition of TBzA + Na_2S, the rate of corrosion remained appreciably lower than that found from the polarization curves for a long time (220 h), and, as can be seen from Table 2, increases with increasing acidity of the solutions. It should be noted

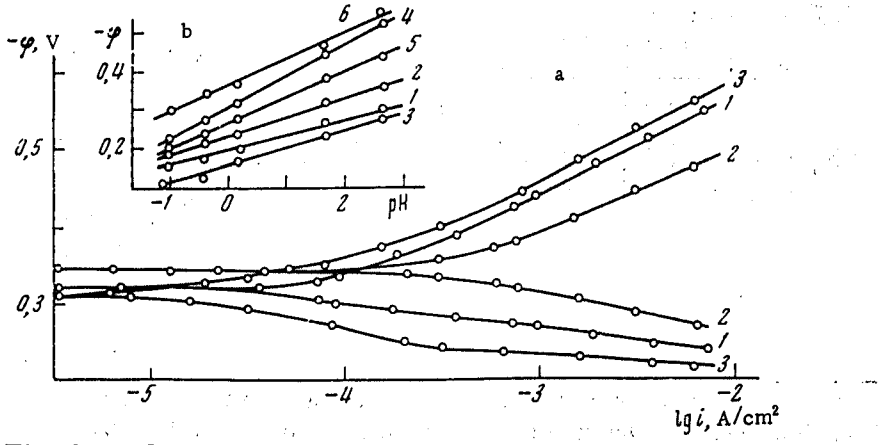

Fig. 2. Polarization curves (a and b): dependence of the anodic (1-3) and cathodic (4-6) potentials on the pH at i = 10^{-3} A/cm^2 in a pure solution of 0.1 N H_2SO_4 + 0.9 N Na_2SO_4 (1, 4) and with additives: (2, 5) 10^{-4} N Na_2S; (3, 6) 10^{-4} N Na_2S + 10^{-4} M TBzA.

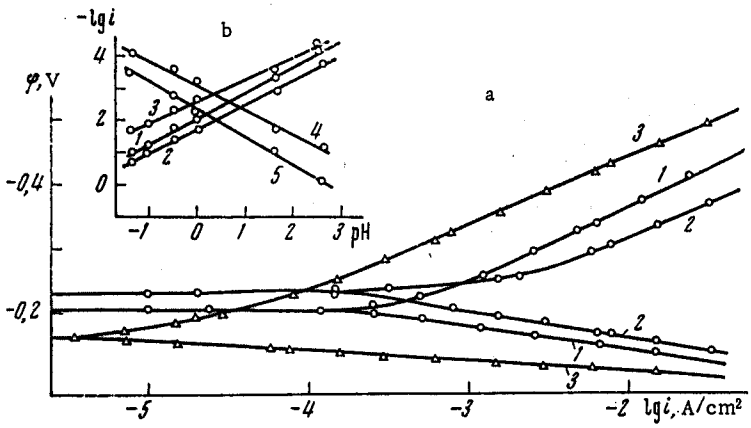

Fig. 3. Curves of the polarization of iron (a) and dependence of the logarithm of the current density of the cathodic reaction on the pH (b) in pure solutions of 3 N H_2SO_4 (1, 4) and with additives: 2, 5) 10^{-4} N Na_2S; 3) 10^{-4} N Na_2S + 10^{-4} M TBzA at $\varphi = -0.4$ V for the cathodic reaction and $\varphi = -0.2$ V for the anodic reaction.

that the inhibitor TBzA in a concentration of 10^{-4} M does not prevent embrittlement of iron, arising in the presence of 10^{-4} N H_2S and increasing with increasing acid concentration and time of corrosion [2].

The acceleration of the cathodic reaction of discharging of hydrogen ions by hydrogen sulfide was explained by the action of the surface catalyst of HS^- anions adsorbed on iron [3]. The concentration and activity of the catalyst increases with increasing negative potential and hydrogen sulfide concentration but drops with increasing pH; therefore the rate of the cathodic reaction decreases with increasing pH more slowly than in solutions without hydrogen sulfide (see Fig. 3b and Table 1).

The acceleration by hydrogen sulfide of the anodic reaction of ionization of iron is also induced by the action of the catalyst, in this case of chemisorbed HS^- anions [4, 5]. The increase in the dependence of $\partial \log i_a / \partial pH$ on the addition of hydrogen sulfide (see Fig. 3b and Table 1) is associated with an increase in the adsorption of HS^- ions on iron with decreasing acidity of the solution and the strengthening of their bond to iron as the potential is displaced in the positive direction, which occurs with decreasing pH. This should lower the activity and the effect of the anodic catalyst.

The slowdown of the cathodic reaction by a cationic-type inhibitor in the presence of a stimulator, hydrogen sulfide, occurs, on the one hand, as a result of the disappearance of the action of the cathodic catalyst in the case of the adsorption of particles of the inhibitor on it in place of protons, and on the other hand, as a result of the appearance of a positive ψ_1-potential, leading to a slowdown of the reaction of discharging of hydrogen ions [3, 5].

The slowdown of the anodic reaction by an inhibitor is caused by blockage of the action of the anodic catalyst indicated above when particles of the inhibitor are adsorbed on its surface and also as a result of the appearance of a positive adsorption potential, creating a supplementary barrier in the escape of iron cations into solution. Thus, inhibitors eliminate the action both of cathodic and of anodic catalysts. The HS^- anions adsorbed on iron serve as anionic bridges, which substantially promote the adsorption of onium-type inhibitors. The explains the strong synergistic effect of the action of inhibitors together with hydrogen sulfide on the corrosion of iron in acid solutions [6, 7].

LITERATURE CITED

1. Z. A. Iofa and Fan Lyong Kam, Élektrokhimiya, 7, 697 (1972).
2. I. S. Shparberg and A. V. Shreider, Zashchita Metallov, 6, 343 (1970).
3. Le Boucher, Rev. Inst. Franç. Petrole, 18, 1-66 (1963).
4. Z. A. Iofa and Wey Bao Min, Catalytic Reactions in the Liquid Phase [in Russian], Izd. AN KazSSR, Alma-Ata (1963), p. 137.
5. Z. A. Iofa, Zashchita Metallov, 6, 491 (1970); 10,17 (1974).
6. Z. A. Iofa, Zashchita Metallov, 8, 139 (1972).
7. Salekh Fuad Khasan and Z. A. Iofa, Zashchita Metallov, 6, 231 (1970).