EFFECT OF pH OF SOLUTIONS ON CORROSION OF IRON AND ACTION OF INHIBITORS

Z. A. Iofa and Fang Lêong K'am

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In [1] it was shown that the effect of inhibitors on the rate of electrochemical reactions and the corrosion rate decreases with increase in the pH value of sulfuric acid solutions with various concentrations and of solutions of sodium sulfate in sulfuric acid with constant ionic strength but different pH values.

The present work gives the results from an investigation of the effect of potassium iodide and tetrabutylammonium iodide (TBAI) in solutions containing 0.1 mole/kg of perchloric acid with the addition of 1, 4, 8, and 15 mole/kg of sodium perchlorate over a wide range of active acidity (from −2 to 2 pH) but with a constant analytical concentration of hydrogen ions [2]. (A pH value of 2.1 was obtained in a solution of 0.1 M $HClO_4$ + 1 mole/kg Na_2SO_4.) In these solutions the stationary cathodic and anodic curves were recorded by the galvanostatic method, and the relative adsorption of the inhibitors on zone-melting iron was determined by measuring the differential capacitance of the double layer in alternating current with a frequency 800 Hz. The pH values of the solutions were measured before and after the experiments by means of a hydrogen electrode in the same cell as the iron electrode. The pH values were similar to the data obtained by Schwabe [2] in similar solutions. The potentials are referred to the saturated calomel electrode. The measured potentials were corrected for the diffusion potentials calculated by the Henderson equation.

From the polarization curves, some of which are presented in Fig. 1, it is seen that the effect of TBAI addition on the rate of the cathode and anode reactions is considerably greater in a solution with a lower pH value.

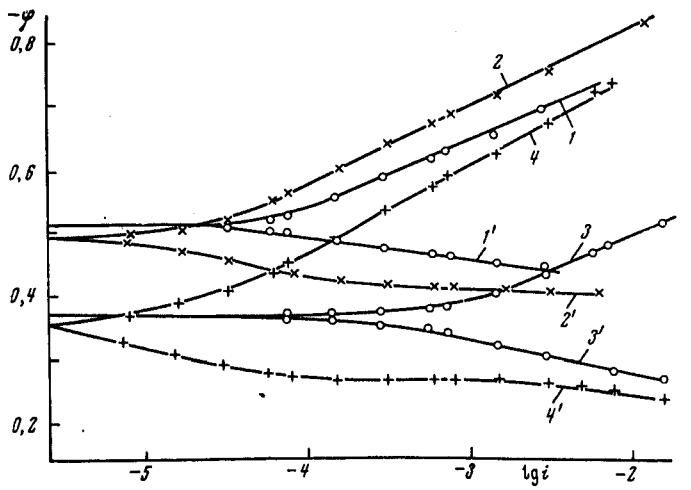

Fig. 1. Cathodic and anodic polarization curves for iron electrode in solutions: 1, 1') 0.1 mole/kg $HClO_4$; 2, 2') the same + 10^{-4} M TBAI; 3, 3') in solution of 0.1 mole/kg $HClO_4$ + 8 mole/kg $NaClO_4$; 4, 4') the same + 10^{-4} M TBAI.

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TABLE 1

0,1 M $HClO_4$ + 1 mole/kg $NaClO_4$	pH	φ = −0,8 V			φ = −0,7 V			φ = −0,55 V		
		C_0, μF/cm²	+ 10^{-4} M TBAI		C_0, μF/cm²	+ 10^{-4} M TBAI		C_0, μF/cm²	+ 10^{-4} M TBAI	
			C	ΔC		C	ΔC		C	ΔC
0	1	37	31	6	41	36,5	4,5	57	44	13
1	0,46	42	38	4	41	35	6,0	49	34	15
4	−0,31	46	40	6	40	33,5	6,5	46	16,1	29,9
8	−1,4	42	33	9	40	25	15	45	13,9	31,1

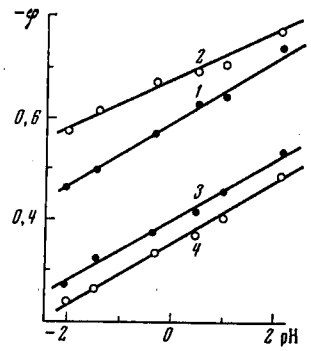

Fig. 2

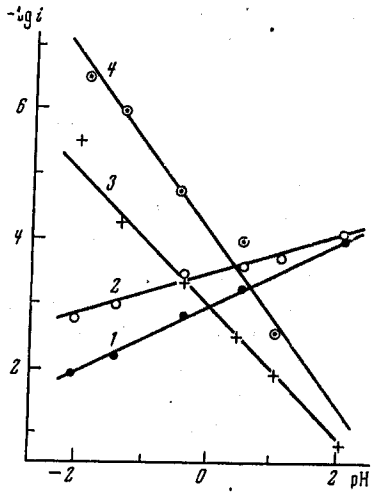

Fig. 3

Fig. 2. Dependence of cathode potential on pH for $i = 10^{-3}$ A/cm² (1 and 2); dependence of anode potential on pH for $i = 10^{-3}$ A/cm² (3 and 4); 1, 3) solutions of 0.1 mole/kg $HClO_4$ + $NaClO_4$; 2, 4) the same + 10^{-4} M $N(C_4H_9)_4I$.

Fig. 3. Dependence of logarithm of cathode reaction rate on pH for $\varphi = -0.6$ V (1 and 2); 3, 4) the same for the anode reaction for $\varphi = -0.45$ V; 1, 3) in solutions of 0.1 mole/kg $HClO_4$ + mole/kg $NaClO_4$; 2, 4) the same + 10^{-4} M $N(C_4H_9)_4I$.

The dependence of the equilibrium potential φ_e on pH, obtained from the polarization curves for solutions without inhibitor, gives a straight line with a slope ($\partial\varphi_e/\partial pH = 0.058$ V) characteristic of the potential of a reversible hydrogen electrode but displaced by approximately 200 mV towards more negative potentials, which is consistent with [3, 4]. In solutions with additions of TBAI or potassium iodide this relationship is also similar to the relationship for the hydrogen electrode.

The potential for the discharge of hydrogen ions φ_c increases linearly with increase in the pH value within the limits of the deviations in the individual experiments (for $i = 10^{-3}$ A/cm², $\partial\varphi_c/\partial pH = -81$ mV) (Fig. 2). Addition of potassium iodide or TBAI changes the factor to −46 and −42 mV, respectively. The decrease in the dependence of φ_c on pH is due to the greater adsorption of the inhibitor and, accordingly, the greater increase in the hydrogen overpotential in solutions with lower pH values. It should be noted that tetrabutylammonium sulfate does not give this effect. Evidently, by being chemisorbed on the surface of the iron, the I^- ions which appear during the dissociation of $N(C_4H_9)_4I$ play the part of anionic bridges promoting the adsorption of $N(C_4H_9)_4^+$ cations, and this leads to the observed synergistic effect [5].

Accordingly the rate of the cathode reaction at constant potential decreases with increase in the pH value. In solutions without inhibitor $\partial \log i_c/\partial pH = -0.5$ A/cm² (Fig. 3). (The $\log i_c$ values were obtained from the polarization curves for $\varphi_c = -0.6$ V.) Addition of potassium iodide or TBAI significantly reduces the value of this relationship to −0.38 and −0.275, respectively. At pH > 2 the inhibitors employed become little effective. The observed decrease in the action of the inhibitors with increase in the pH is clearly due to competition with the chemisorbed OH^- ions, the increase in the surface concentration of which with

increase in pH leads to displacement of the inhibitor from the iron surface, as was indicated in [6]. As known, the ionization rate of iron increases with increase in the pH value owing to an increase in the surface concentration of $(FeOH)_{ads}$ [7, 8].

With increase in the pH value the anode potential φ_a for i = const is shifted by about 60 mV towards more negative values in solutions both without inhibitor and with the addition of TBAI (Fig. 2), while the rate of the anodic reaction for φ_a = const increases accordingly (Fig. 3). In solutions without inhibitor $\partial \log i_a / \partial pH = 1.0$ (first order in OH^- ions). Addition of TBAI leads to a significant decrease in the rate of the anodic process but with an intensification of its dependence on pH: $\partial \log i_a / \partial pH = 1.25$ A/cm^2.

The differential capacitance curves recorded in the solutions (converted to the parallel capacitance –resistance circuit) indicate an increase in the adsorption of the inhibitors with decrease in the pH value of the solutions (Table 1).

The capacitance of the electrode in solutions without inhibitor C_0 increases with the addition of $NaClO_4$ salt for negative charges on the electrode surface and decreases for positive charges, and the φ, C curves intersect at $\varphi = \sim -0.7$ V (~ -0.45 V referred to the normal hydrogen electrode) in the region close to the potential of zero charge for the iron surface (0.37 to –0.4 V [9]), like the effect observed in the case of the mercury electrode [10].

With decrease in the negative potential or charge of the electrode surface in solutions containing both TBAI and potassium iodide there is a decrease in the capacitance and, consequently, an increase in the adsorption, which in this case is due to an increase in the primary adsorption of the I^- ions, promoting (as mentioned above) the adsorption of inhibitors of the cationic type.

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