BRIEF COMMUNICATIONS

INFLUENCE OF pH ON THE ELECTROCHEMICAL REACTIONS INVOLVED IN THE CORROSION OF IRON IN THE PRESENCE OF INHIBITORS

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The influence of pH on the electrochemical reactions of hydrogen ion discharge and the ionization of iron, which determine the process of corrosion in the absence of oxidizing agents, has been studied by a number of workers, but the pH dependence of the action of surface-active agent inhibitors on these reactions has been studied in insufficient detail.

In the present work we studied these reactions for pure zone-fusion (ZF) iron in $H_2SO_4 + Na_2SO_4$ solutions with a total concentration of 1 N in the pH range from 0.3 to 2.74 (system 1) and on Armco iron in the H_2SO_4 solutions with concentrations in the range 0.01-10 N (system 2). We recorded the polarization curves under steady-state conditions and the differential capacity curves, using alternating current. The pH of the solutions was measured before and after the experiment, directly in the measuring cell, by means of a hydrogen electrode. The iron electrodes were annealed beforehand at 600°. In all cases the experiments were repeated two or three times, and the mean values are given in the text. The potentials are given with respect to a saturated calomel electrode (φ = 0.252 V with respect to the normal hydrogen electrode). The temperature of the experiments was 20 ± 1°C. As surface-active substances (SAS) we used $4 \cdot 10^{-4}$ N $[N(C_4H_9)_4]_2SO_4$ (TBAS), $4 \cdot 10^{-4}$ N, KI, and $4 \cdot 10^{-4}$ N $N(C_4H_9)_4$ (TBAI) in the case of system 1, and 10^{-4} M $N(C_6H_5CH_2)_3$ (TBzA), 10^{-4} N KI, and their mixture 10^{-4} M TBzA + $1 \cdot 10^{-4}$ N KI in the case of system 2.

The polarization curves, some of which are given in Fig. 1, show that the effect from the addition of inhibitors at high pH values is very small: there is a slight displacement of the cathodic potential (φ_c) towards more negative values, and of the anodic (φ_a) and steady-state (φ_s) potentials towards more positive values. At lower pH values these effects are much more marked.

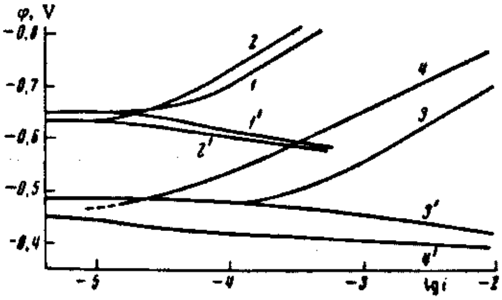

Fig. 1. Cathodic and anodic polarization curves (φ, log i) for a zone-fusion electrode in $H_2SO_4 + Na_2SO_4$ solutions containing 1N SO_4^{2-}; pH values: 1,1') 2.74; 3,3') 0.31; 2,2' and 4,4') + $4 \cdot 10^{-4}$ N tetrabutylammonium iodide.

In $H_2SO_4 + Na_2SO_4$ solutions (system 1) φ_s is displaced towards more negative values with increase in pH: $\partial\varphi_s/\partial pH = -58$ mV. In the presence of inhibitors (KI and TBAI) this coefficient increases to 65-75 mV due to an increase in the inhibiting effect with decrease in the pH of the solutions. The pH dependence of φ_s in pure solutions is close to the pH dependence of the hydrogen electrode, but the entire φ_s, pH straight line is displaced by 200 mV towards more negative values, in agreement with published data [1, 2].

In H_2SO_4 solutions on Armco iron, $\partial\varphi_s/\partial pH = -48$ mV, and the φ_s, pH straight line is also displaced by 220 mV relative to the straight line for the hydrogen electrode. In solutions with added KI and TBzA + KI, $\partial\varphi_s/\partial pH$ lies between −60 and −65 mV.

The rate of the spontaneous dissolution of ZF iron decreases slightly with increase in pH: $\partial \log i_s/\partial pH = -0.38$

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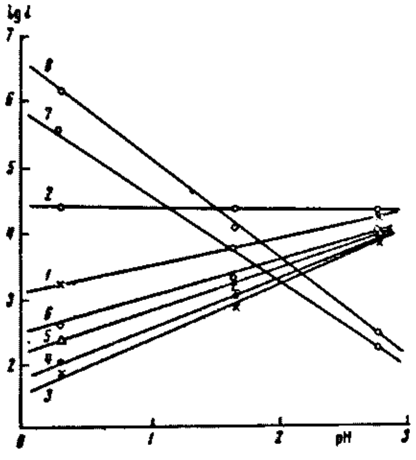

Fig. 2

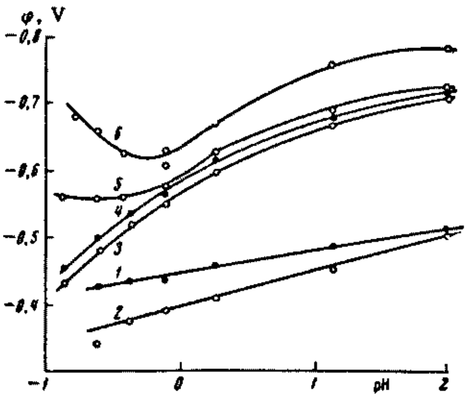

Fig. 3

Fig. 2. Curves giving the pH dependence of: log i_s (1, 2); log i_c (3-6); log i_a (7, 8); 1, 3, 7) in pure $H_2SO_4 + Na_2SO_4$ solutions; 4) + TBAS; 5) +KI; 2, 6, 8) +TBAI. log i_c at $\varphi = -0.70$, log i_a at $\varphi = -0.55$ V. Zone-fusion iron.

Fig. 3. Curves giving the pH dependence of: φ_a (1, 2); φ_c (3-6); 1 and 3) in pure H_2SO_4 solutions; 4) $+10^{-4}$ M tribenzylamine; 5) $+10^{-4}$ N KI; 2 and 6) $+ 10^{-4}$ M tribenzylamine $+10^{-4}$ N KI; φ_c and φ_a at $i = 10^{-3}$ A/cm². Armco iron.

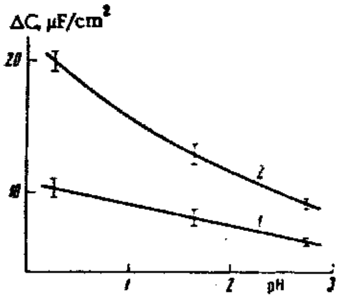

Fig. 4. pH dependence of the decrease in the differential capacity of the double layer for $H_2SO_4 + Na_2SO_4$ solutions on addition of the inhibitors: 1) $4 \cdot 10^{-4}$ N KI; 2) $4 \cdot 10^{-4}$ M TBAI.

TABLE 1

pH	Solution	lg i_a	Solution	lg i_a
2	H_2SO_4	−4,2	$H_2SO_4 + Na_2SO_4$	−3,2
1	The same	−5,2	The same	−4,5

A/cm² (curve 1 in Fig. 2). The addition of TBAI alters the sign of the relationship: $\partial \log i_s/\partial pH = 0.07$ A/cm² (curve 2 in Fig. 2).

The cathodic potential for the liberation of hydrogen on zone-fusion Fe with increase in pH in displaced linearly towards more negative values: $\partial\varphi_c/\partial pH = -120$ mV. This dependence corresponds to the requirements of the theory of retarded discharge in solutions with ψ_1 = const. The addition of KI and TBAI leads to a decrease in this coefficient as a consequence of the increase in the retardation of the reaction of the inhibitor with decrease in pH, to −85 and −77 mV respectively. At $i = 10^{-3}$ A/cm² and pH = 0 the cathodic potential in the pure solution is −475 mV; the addition of TBAS, KI, and TBAI increases it to −510, −610, and −640 mV. In accordance with the change in φ_c with change in pH, there is a change in the rate of liberation of hydrogen. In pure $H_2SO_4 + Na_2SO_4$ on ZF iron, $\partial \log i_c/\partial pH = -0.8$; in a solution with added TBAS, KI, and TBAI, this coefficient decreases to −0.73, −0.61, and −0.51 A/cm². It can be seen from curves 3-6 in Fig. 2 that the retarding action of the additives on the cathodic reaction at high pH values increases significantly with decrease in pH.

In H_2SO_4 solution on Armco iron (system 2), the φ_c, pH curve deviates from a straight line (curve 3 in Fig. 3). In the range of H_2SO_4 concentrations from 0.01 to 0.1 N, $\partial\varphi_c/\partial pH = -55$ mV. This value in the range of low concentrations of the pure acid is apparently related to a change in the diffusivity of the double layer and a change in the ψ_1-potential with change in concentration. With increase in the concentration of acid from 1 N, the slope of the φ_c, pH curve increases (curve 3 in Fig. 3). In this range of acid concentrations, the diffusivity of the double layer remains almost unchanged, but $\partial\varphi_c/\partial pH > -120$ mV; this is evidently due to the accelerating action of adsorbed SO_4^{2-} anions on the liberation of hydrogen, as for example in the case of mercury and lead cathodes [3]. The φ_c, pH curve for the solution with added TBzA (curve 4) passes close to the curve for the pure acid solution. The addition of KI and TBzA + KI alters the course of the φ_c, pH curve: a minimum is observed at ~3 N H_2SO_4, and further increase in the H_2SO_4 concentration leads to an increase in φ_c and a change in the sign of the coefficient $\partial\varphi_c/\partial pH$ (curves 5 and 6 in Fig. 3). The increase in φ_c with increase in the H_2SO_4 concentration is probably due to an increase in the adsorption of the inhibitor. In this case the SO_4^{2-} ions act as anionic bridges, facilitating the adsorption of inhibitors of the cationic type [4].

It must be assumed that the observed decrease in the action of inhibitors with increase in pH in solutions with a constant concentration of SO_4^{2-} ions is due to an increase in the surface concentration of OH^- ions, which are able to displace the SAS, for example I^- ions, from the iron surface, as pointed out in [5].

The kinetics of the anodic dissolution of iron also depend markedly on the pH of the solutions [6, 7]. The experiments showed that the anodic potential decreases linearly with increase in pH. In H_2SO_4 + Na_2SO_4 solutions on ZF iron, $\partial\varphi_a/\partial pH = -48$ mV. The addition of KI + TBAI increases this coefficient to 60 mV.

The rate of the anodic reaction increases with increase in pH: $\partial \log i_a/\partial pH = 1.35$ A/cm². In solutions with added TBAI, $\partial \log i_a/\partial pH = 1.57$ A/cm² (curves 7 and 8 in Fig. 2).

A qualitatively analogous picture is observed in the case of Armco iron in H_2SO_4 solutions: $\partial\varphi_a/\partial pH = -35$ mV, $\partial \log i_a/\partial pH = 1.02$ A/cm² in pure H_2SO_4 solutions, and $\partial\varphi_a/\partial pH = -53$ mV, $\partial \log i_a/\partial pH = 2.3$ A/cm² in solutions with added TBzA + KI.

The increase in the rate of ionization of iron with increase in pH is due to the reaction of its surface atoms with OH^- ions and the catalytic action of the adsorption compound $(FeOH)_{ads}$ formed [7, 8].

A number of workers have shown that the rate of the anodic dissolution of iron depends not only on pH but also on the concentration of other anions present in the solution [9, 10].

Comparison of the log i_a values for the same pH value and $\varphi_a = -0.55$ V from the results of our experiments in systems 1 and 2 gave a result which indicated that the addition of Na_2SO_4 to H_2SO_4 solution increases the rate of the ionization of iron by almost one order of magnitude (see Table 1).

To prove that the pH influences the adsorption of the SAS, we recorded the differential capacity curves using alternating current. The value of the capacity, measured by a capacity–resistance series scheme, was recalculated for the parallel scheme. The frequency of the alternating current was 800 Hz. The capacity in pure H_2SO_4 + Na_2SO_4 solution on ZF iron was 40 μF/cm². Curves giving the pH dependence of the decrease in capacity (ΔC) on the addition of the SAS (1) $4 \cdot 10^{-4}$ N KI; 2) $4 \cdot 10^{-4}$ M $N(C_4H_9)_4I$) are given in Fig. 4. It can be seen from the curves that the decrease in capacity in the presence of the added SAS increases with decrease in the pH of the solutions, indicating an increase in their adsorption with increase in the concentration of acid in the solution.

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