IRON PASSIVATION POTENTIAL AND SOLUTION COMPOSITION

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Different dependences of the iron passivation potential on the compositions of aqueous solutions with different anions are reported. The idea that passivation processes can be reduced to reactions in the system Fe—H_2O is shown to be wrong.

INTRODUCTION

Empirical pH dependences of the plateau potential (or the potential at the end of the plateau) on the E(t) curves obtained after the passivating anodic current is shut off (or after replacement of a passivating solution by a nonpassivating one) are often brought into the discussion of the mechanism of iron passivation. The plateaus are assumed to be associated with reactions in which the passivating layer is reduced. Such equations were obtained by Franck [1] for the 0.3-4.02 pH range (potentials are with respect to the normal hydrogen electrode),

$$E_F = 0.58 - 0.058\ \text{pH}, \quad (1)$$

by Sukhotin and Kartashova [2] for the 0.3-4.7 pH range,

$$E_F = 0.58 - 0.1\ \text{pH}, \quad (2)$$

and by Nagayama and Cohen for borate solutions with pH 6-9,

$$E_F = 0.958 - 0.163\ \text{pH} - 0.06\log[Fe^{2+}]\ . \quad (3)$$

In several cases, however, the plateaus have no direct relation to the reduction of the passive layer, and are caused by "side" electrochemical reactions [4]. On the other hand, there is no doubt that if the plateau is caused by the reduction of a passivating layer, the mechanism for this process when E is decreased is the same as the passivation-activation mechanism during the recording of anodic E(i) polarization curves.

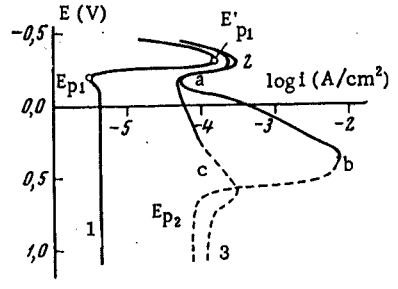

Fig. 1. Anodic polarization curves of Hilger iron in a pure borate solution (1) and with 0.1 N Na_2SO_4 (2) and 0.1 N $NaClO_4$ (3). The pH was 7.4 in all cases, and the average potential shift rate was 6.25 mV/min. The dashed lines show the inadequate quantitative reproducibility of the curves.

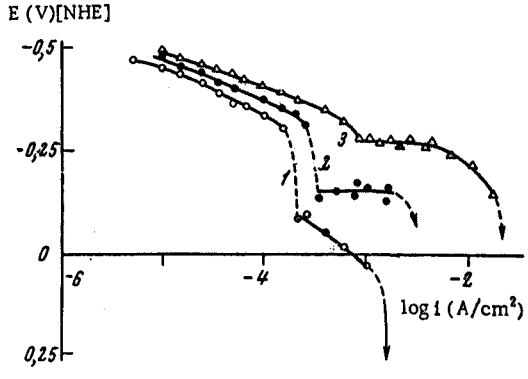

Fig. 2. Galvanostatic polarization curves of Hilger iron in a borate solution with added Na_2SO_4. 1) 0.01; 2) 0.1; and 3) 1.0 N Na_2SO_4.

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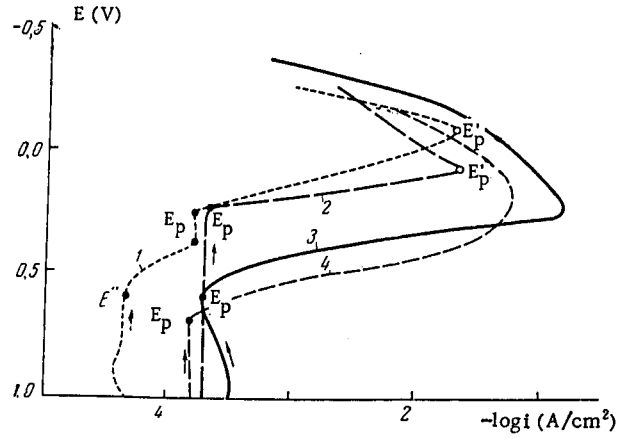

Fig. 3. Anodic polarization curves for iron in the solutions $H_nX + Na_nX$ at pH 4.5 and [X] = 1 N. 1) $NaNO_3 + HNO_3$; 2) $CH_3COONa + CH_3COOH$; 3) $Na_2SO_4 + H_2SO_4$; 4) $NaClO_4 + HClO_4$

The empirical equations (1) and (2) were obtained experimentally without provision for holding constant the anion content in the solution. The propriety of such a means of measurement has not been confirmed by special experiments. One cannot therefore accept the idea that several inorganic anions (SO_4^{2-}, NO_3^-, etc.) are inert with respect to iron passivation, and that this process is entirely attributable to some reactions in the $Fe-H_2O$ system. This idea is contradictory to data on the significant specific adsorption of SO_4^{2-} ions on passivating metals [5] (including the shielding of Cl^- ions by SO_4^{2-} ions) and on the ability of these ions (often much greater than for Cl^- ions) to disrupt the iron passive state [6-8].

In agreement with the data of [3, 9], we found [10-13] that the potentiostatic anodic curve for Fe has one current maximum in pure borate solutions. The potential E'_{p_1}, which corresponded to this maximum, decreased significantly with increasing pH, and within the experimental error was independent of the concentration of several inorganic anions, but differed sharply from the value E_F calculated from Franck's equation (1). When SO_4^{2-} and ClO_4^- ions were added, a second current maximum appeared (in about the 0.4-0.8 V region) on the anodic potentiostatic curve (Fig. 1).* Apparently the iron passive state with $E > E'_{p_1}$ is disrupted by these anions; activation by SO_4^{2-} ions should be very similar to that caused by halide ions. The intense corrosive pitting of the electrodes in the activation region (ab on curve 2 of Fig. 1) and the galvanostatic measurements under conditions close to steady-state, support this argument. When the anodic current increased in the activation region, the E(t) curves had the same shape as during passivation disruption by halide ions [14]. The activation regions of the polarization curves (Fig. 2) plotted from these data for 0.1 and 1.0 N Na_2SO_4 solutions are horizontal over a wide range of i; this could be explained by an increase in the activated surface area proportional to the increase in anodic current [14]. As during activation by halide ions, these regions are shifted toward negative potentials when the sulfate concentration in the solution is increased.

This activation of iron by SO_4^{2-} ions is suppressed at sufficiently high potentials (Fig. 1), in contrast with the case of halide solutions.

The potential E_{p_2}, which corresponds to the boundary of the passive region on the side of negative E, is sharply different from the value E_F, which was also observed during the recording of the anodic curves along the reverse path (from the second passive region toward negative E) in sulfate solutions. In these experiments also, the iron was subjected to severe corrosive pitting in the activation region of the curve: cb in Fig. 1. In general, pitting occurs during the whole potential range corresponding to the second hump in the polarization curve (abc of curve 2 in Fig. 1), as was shown by potentiostatic experiments with prior passivation of the iron in a pure borate solution (pH 7.4) followed by replacement with a Na_2SO_4 solution at the same pH (without interruption of polarization).

* In contrast with our earlier study [10], the ends of the iron wire electrodes were insulated (according to the data of [12]) when we recorded curves 2 and 3 of Fig. 1. With this arrangment, we could record the distortion in the polarization curves in the region from ~−0.3 to ~+0.3 V (which was considerably smaller in Na_2SO_4 solutions than in $NaClO_4$ solutions, but still significant), and obtain clearer data for appraising the activation of iron by SO_4^{2-} ions.

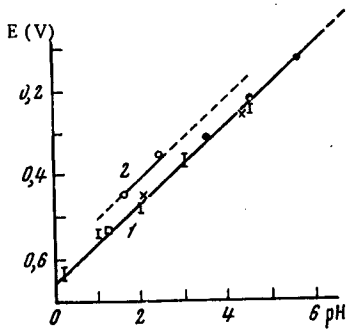

Fig. 4. Dependence of the iron passivation potential in nitrate ($HNO_3 + NaNO_3$) and acetate ($CH_3COONa + CH_3COOH$) solutions on the pH. ○) $[NO_3^-] = 0.1$ N; I) $[NO_3^-] = 1$ N; ×) $[NO_3^-] = 2.46$ N; □) $[NO_3^-] = 7.7$ N; ●) $[Ac^-] = 1$ N.

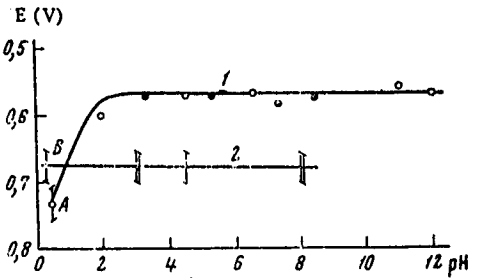

Fig. 5. Dependence of the iron passivation potential on the pH in sulfate (1) and perchlorate (2) solutions. ○) Unbuffered solutions of $Na_2SO_4 + H_2SO_4$ or $Na_2SO_4 + KOH$, $[SO_4^{2-}] = 1$ N; point A) 1 N H_2SO_4; ●) buffered solutions of 1 N Na_2SO_4 (addition of borax and boric acid for pH > 7, or addition of borax and succinic acid for pH < 6); I and II) unbuffered and buffered solutions with $[ClO_4^-] = 1$ N; point B) 1 N $HClO_4$.

The first passivation under steady-state conditions in 1 N Na_2SO_4 solutions was observed only for pH > 7; at lower pH the potential E'_{p_1} shifted towards the region of disruption of the first passivity by SO_4^{2-} ions, and one current maximum, corresponding to the second passivation, remains on the E(i) curve.

The above shows the necessity of determining the effect of the anion composition of the solution on iron passivation characteristics.

METHOD

Cold-drawn wire (d = 1 mm) of pure iron, vacuum-melted and poured in an argon atmosphere, was used for the electrodes. The wire composition was, in %: 99.94 Fe, 0.005 C, 0.03 Si, 0.02 Mn, 0.004 S, and 0.001 P. The initial reactants were as a rule further purified by recrystallization (salts) or distillation (acids); the solutions were prepared from doubly-distilled water.

An electronic potentiostat with a response time of $< 10^{-4}$ sec was used for the polarizations. The experiments were conducted in an atmosphere of purified nitrogen in a three-electrode cell at 20 ± 1°C.

The majority of experiments were conducted as follows.

The electrode was cleaned with a corundum abrasive, degreased with ethyl alcohol, washed in doubly-distilled water and etched for 5 min in 1N H_2SO_4 or $HClO_4$. It was then rinsed in doubly-distilled water, connected to the potentiostat, and immersed in the solution with the potential fixed in the passive region. After a relative stabilization of the current, a polarization curve was recorded by shifting the potential in the negative direction in 20 mV steps with 2 min delays at each potential (the average shift rate was $V_{sh} = 10$ mV/min). It was shown in special experiments that a decrease in V_{sh} to 2 mV/min did not affect the magnitude of E_p, so the values obtained for E_p can be taken as steady-state.

The reproducibility of the currents in the passive region was inadequate for a discussion of the solution-composition dependence of the passive-iron dissolution rate. It was observed, however, that the current did not affect the passivation potential E_p. The data of Flade [15] (determination of E_F) and Hines and Williamson [16] confirm this effect in sulfuric acid solutions. Values of E_p reproducible within 20 mV are shown by points on the graphs; in other cases, the scatter is indicated.

Experiments were conducted at room temperature with a 1 N solution of Na_2SO_4 tagged with the β-isotope S^{35} to follow the potential dependence of SO_4^{2-} adsorption on iron. The sample (15 × 15 × 0.5 mm) was held in the tagged solution for 2 h at the given potential; the sample activity was measured by an end-window

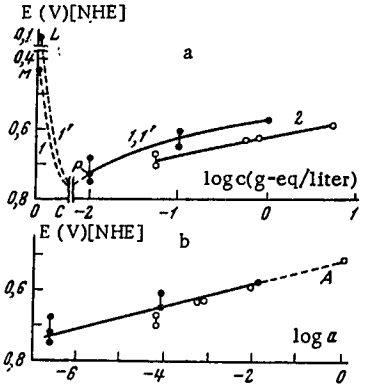

Fig. 6

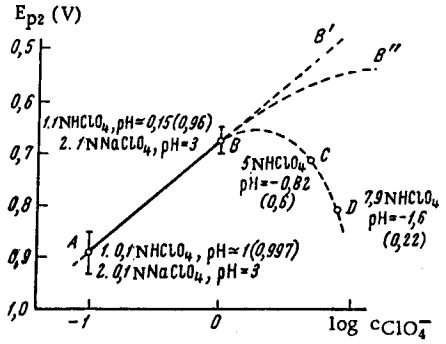

Fig. 7

Fig. 6. a) Dependence of E_p on the Na_2SO_4 concentration in background buffer solutions at pH 3.3 (1), pH 5.3 (1'), and on the $CdSO_4$ concentration (2); the points L and M represent E_p in pure background solutions (borax + succinic acid), $[SO_4^{2-}] = 0$; while the point P represents the most probable value of E_p in 0.01 N Na_2SO_4; b) dependence of E_p on the sulfate activity; ●) Na_2SO_4; ○) $CdSO_4$.

Fig. 7. Dependence of E_p on the ClO_4^- concentration in $NaClO_4$ and $HClO_4$ solutions. The vertical bars at points A and B represent the scatter in the data. The solution compositions are shown near each point. The numbers in parentheses are the activity of water in the $HClO_4$ solutions, according to calculations by E. V. Kasatnik.

detector; there were strictly standardized conditions for washing the sample (with distilled water) and drying it (with ethyl alcohol). To eliminate the effects of sulfate sorption by corrosion products, which was very important near the maximum current of the E(i) curve, we measured the activity on samples which were polarized briefly (5 min) and rinsed with deaerated distilled water in the cell immediately after the polarization was interrupted. Depending on the reproducibility of the data, 3-10 samples were used.

RESULTS

In the majority of cases, the E(i) curves obtained had a comparatively simple shape, with one passivation potential E_p (Fig. 3). In nitrate solution with pH≳1.5 (Fig. 3, curve 1), however, the current increase with potential decrease begins at poorly reproducible, and thus not examined, values of E = E" in the region between 0.15 and 0.55 V. This curve had the same shape as the anodic polarization curve for the forward path in 5 N NH_4NO_3 with pH 4.8, obtained by Mieluch [17]. No current increase was observed in the potential range studied for the 1 N Na_2SO_4 + KOH solution with pH 12.4. It can be concluded that iron is not activated by SO_4^{2-} ions when $[SO_4^{2-}] = 1$ N and at pH ≥ 12.4; this conclusion is in agreement with the results of [18].

The results of the E_p measurements in nitrate solutions, shown as a function of the pH in Fig. 4, can be described by

$$E_p = 0.66 - 0.1\,\mathrm{pH} + k\log[NO_3^-] \qquad (4)$$

where

$$k = 0.06 \text{ at } [NO_3^-] = 0.1 - 1.0 \text{ N};$$

$$k = 0 \text{ at } [NO_3^-] \geqslant 1.0 \text{ N}.$$

Figure 4 also shows that the points for E_p in acetate solutions with $[Ac^-] = 1$ N lie along curve 1. Taking into account the data on the effect of the Ac^--ion concentration on E_p at pH 4.5 (in the $[Ac^-]$ range from 0.05 to 5.0 N), we can write for acetate solutions:

$$E_p = 0.66 - 0.1\,\mathrm{pH} + 0.03\log[Ac^-]. \qquad (5)$$

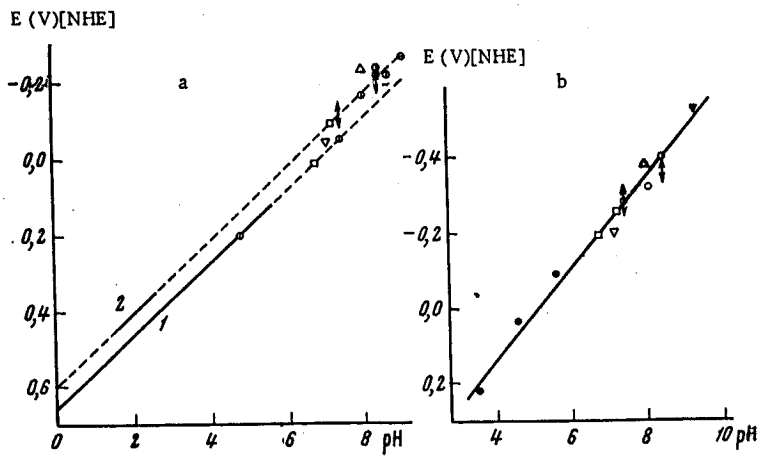

Fig. 8. Comparison of the pH dependence of E_{p_1} (a) and E'_{p_1} (b) obtained in this study with those from the literature. Curves 1 and 2 are from Eqs. (8) and (9). ◊) 5 N solution of NH_4NO_3 [17]; □) NaAc + HAc, $[Ac^-] = 1$ N [19]; ▽) borate solution [20]; ↕) borate solution (this study); ○) borate solution [21]; ◑) borate solution [3]; ⊖) borate solution [22]; △) borate solution +0.2 N NO_3^- [8]; ▼) borate solution [9]; ●) NaAc + HAc, $[Ac^-] = 1$ N (this study). The solid lines show the regions in which points were obtained in this study.

Special experiments showed no effect of Fe^{2+} ions on the potentials E_p and E'_p in a nitrate solution at pH 3.0

As is seen in Fig. 5, the value of E_p with $[SO_4^{2-}] = 1$ N does not depend on the pH in the pH range 2-12 in Na_2SO_4 solutions. The data for 5.7 and 0.057 N $CdSO_4$ solutions in the pH range 3-5 support this conclusion. The possibility that this effect is associated with the establishment in a near-electrode layer of a constant pH, independent of the pH in the bulk solution, is excluded for the following reasons: 1) the value of E_p is the same in buffered and unbuffered solutions (Fig. 5); 2) agitation (in buffered and unbuffered) solutions has no effect on E_p; 3) the pH range in which E_p is independent of the pH is too large (ten pH units); and 4) the passivation potential is found to be clearly dependent on the pH in solutions with other anion compositions, under otherwise equal conditions (Fig. 4).

With these data (Fig. 6a), we can find the decrease in E_p with increased salt concentration in both $CdSO_4$ and Na_2SO_4 solutions. Expressing E_p as a function of the salt activities, we can describe the experimental points for solutions of both salts by a single straight line (Fig. 6b) with the equation

$$E_p = 0.51 - 0.03 \log a, \tag{6}$$

in which a is the molal salt activity. The scatter in the data for dilute sulfate solutions makes determination of the absolute values of the constants in (6) inaccurate, but it does not mask the nature of the dependence. Expressing E_p as a function of the mean ionic activity ($a_\pm$), we get instead of (6) the equation

$$E_p = 0.5 - 0.09 \log a_\pm. \tag{7}$$

In solutions with ClO_4^- ions, the pH also affects the potential E_p (Fig. 5, curve 2), which shifts toward more negative values with increased $[ClO_4^-]$, as in sulfate solutions, if the activity of the water is approximately constant (Fig. 7, region AB).

DISCUSSION

These data show the different behaviors of iron passivation in nitrate and acetate solutions on the one hand; and in sulfate and perchlorate solutions on the other. Accordingly we can assume the existence of two types of iron passivation processes, and use the notation E_{p_1} and E_{p_2} instead of just E_p.

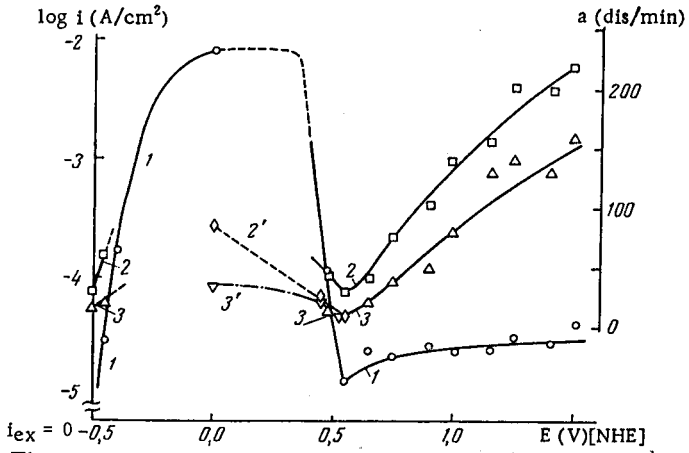

Fig. 9. Potential dependences of several quantities. 1) Anodic current density after polarization for 2 h; 2 and 3) electrode activity after polarization for 2 h, 0.5 and 3.5 min respectively after the standard washing; 2' and 3') sample activity after polarization for 5 min, after washing with deaerated doubly-distilled water in the cell, and after a supplementary standard washing, respectively. The solution was 1 N Na_2SO_4, pH ≃ 6.5.

Passivation of the First Type (Nitrate, Acetate, and Borate Solutions)

Two lines appear in Fig. 8a; the first of these corresponds to the equation

$$E_{p_1} = 0.66 - 0.1\,\mathrm{pH}, \tag{8}$$

which in conjunction with (4) and (5) relates to nitrate solutions with $[NO_3^-] = 1.0$ N and acetate solutions with $[Ac^-] = 1$ N; the second line corresponds to the equation

$$E_{p_1} = 0.6 - 0.1\,\mathrm{pH}, \tag{9}$$

which in conjunction with (4) and (5) relates to nitrate solutions with $[NO_3^-] = 0.1$ N and acetate solutions with $[Ac^-] = 0.01$ N.

Figure 8a also shows literature data for E_{p_1} of nitrate, acetate, and borate solutions, and our data for borate solutions, obtained by recording forward polarization curves. Taking into account the possible influence of different procedures in the different studies, we may assume that iron passivation in neutral borate solutions (see the Introduction) and that in weakly acid or very acid acetate and nitrate solutions occur by the same process. A similar situation is observed for E'_{p_1} the potential at the current maximum in the corresponding pH range; as is evident from Fig. 8b, the E'_{p_1} points corresponding to our and others' data for acetate and borate solutions* lie on a line whose equation is

$$E_{p_1}' = 0.59 - 0.12\,\mathrm{pH}. \tag{10}$$

It is highly probable that the different pre-pH coefficients in Eqs. (4), (5), and (10) are caused by experimental errors, and that in fact

$$\frac{\partial E_{p_1}}{\partial\,\mathrm{pH}} = \frac{\partial E_{p_1}'}{\partial\,\mathrm{pH}} \simeq -0.11 \left(\simeq 2.3 \cdot 2RT/F\right). \tag{11}$$

The strong influence of the pH and the relatively weak influence of anions on the potential E_{p_1}, and the absence (within our experimental error) of anion effects on the potential E'_{p_1}, can be taken as evidence that the first type of passivation is related to the formation of an oxide or oxygen layer during the interaction of iron with water; the completion of this process (at E_{p_1}) may be prevented by sufficiently stably adsorbed anions.

* The data on E'_{p_1} in unbuffered nitrate solutions are different from those shown in Fig. 8b. An analysis shows that the differences may be due to pH changes unique for solutions with NO_3^- ions in a solution layer near the anode, when the current is sufficiently high near E'_{p_1}.

Passivation of the Second Type (Sulfate and Perchlorate Solutions)*

The data of Fig. 5 may be unexpected from the usual point of view about iron passivation, but an analysis of the results of studies known to us [15, 23-25], in which the values of E_p (E_F) for iron† in sulfate solutions were determined for one reason or another, shows that these values are always significantly more positive than predicted by the Franck equation, when pH $\gtrsim$ 2-3. They are also significantly more positive than those values of E_F (E_p) which would be obtained by extrapolation in the pH > 2-3 region of the pH dependences of E_F (E_p) in these studies for solutions of sulfuric acid with pH < 2-3. Judging, for example, from the polarization curves of [23], in which 0.5 N K_2SO_4 was added to 10 N H_2SO_4 solutions (pH −0.47), 1 N solutions (pH 0.56), 0.1 N solutions (pH 1.67), and 0.01 N solutions (pH 2.73), the E_p values of an alloy of Fe+5% Ni turned out to be 0.9, 0.72, 0.6, and 0.6 V, respectively. Such data, which could long ago have shown the independence of E_p from the pH in solutions with SO_4^{2-} ions, received no attention in the papers cited.

The simplest qualitative explanation of the independence of E_{p_2} from the pH would be that near E_{p_2} the bond of the adsorbed anion with the iron is greatly strengthened, and the corresponding surface complex does not disintegrate, becoming a passivator. In this case, the second type of passivation may be associated with the reversible reaction

$$Fe + nSO_4^{2-} = [Fe(SO_4)_n]_{ads} + 2ne. \quad (12)$$

This explanation is, however, contradicted by the following.

a) If it were correct, one would expect a significant increase of stable anion adsorption as E_{p_2} is approached from more negative potentials. As the data of Fig. 9 show, an actual drop in the electrode radioactivity is observed in this case for electrodes polarized in the tagged sulfate solution; at $E = E_{p_2}$, the adsorption is approximately the same as at the self-dissolution potential.

This shape of the adsorption curve reminds one of the well-known data [26] on desorption of sulfuric acid from platinum in the potential range for oxygen deposition.

b) When there is direct passivation by anions in a reaction of the type (12), the iron should also be passivated in the corresponding nonaqueous solutions. In our experiments, however, we could not passivate iron in a 1 N solution of sulfuric acid in methanol, which indicates that water is required for the second type of passivation.

c) If this passivation were caused by a reaction of the type (12), the dependence of E_{p_2} on $[ClO_4^-]$ would have the form ABB' or ABB" (Fig. 7). In fact, one obtains the curve ABCD with a maximum corresponding to the start of a significant decrease of the water activity with increasing $[HClO_4]$.

It can accordingly be assumed that the reason for the second type of passivation is also the formation of an oxide or oxygen layer on the iron surface; the donor of the passivating oxygen is water. Taking into account the data of Fig. 5a and Eq. (6), one sees that this assumption makes it very difficult to consider the second type of passivation as a reaction occurring under equilibrium conditions, ‡ and apparently requires the approach used in the so-called kinetic theories of passivation [29]. In such an approach, one assumes that the anions SO_4^{2-} and ClO_4^- accelerate the formation of the passivating layer (as several anions accelerate active dissolution [30]) in order to theoretically derive the observed dependences of the passivation potential on the solution composition. These anions could, for example, be assigned the role of oxygen

* It should be kept in mind that passivation of the first type also occurs in such solutions under certain conditions (Fig. 1).

† The data of [24] refer to the potential at maximum current, which the authors of [24] denote by E_2.

‡ The difficulty follows if one assumes, following Franck, Sukhotin, and many other authors, that the passivation characteristics are governed directly by the solution of the bulk solution. The views of V. M. Novakovskii [27] (see also [28]) suggest another approach, according to which active or partially active centers on the metal surface should play an important role in the electrochemical behavior of a passive metal. If such centers exist long enough that the solution composition nearby is considerably changed, the passivation potential can have only an indirect dependence on the composition of the bulk solution.

carriers from the water molecule to the metal, in connection with the difficulties associated with a direct interaction of the water with metal atoms on a surface covered by adsorbed anions.

Without regard to the particular theory adopted, it follows from the data above and Eq. (6) that SO_4^{2-} anions, which disrupt the first passive state at sufficiently negative potentials, aid iron passivation near E_{p_2}. Such a change in the effect of the anion is, generally speaking, not unexpected. Popov and Kabanov [7] showed earlier that several anions (OH^-, SO_4^{2-}, Cl^-) act as iron activators at certain potentials in alkaline solutions, and as iron passivators at other potentials.

A comparison of curves 1 and 2 of Fig. 5 shows that E_{p_2} is 0.1 V higher in solutions with $[ClO_4^-] = 1$ N than in solutions with $[SO_4^{2-}] = 1$ N. The value of E_{p_2} does not change in the transition from 1 N salts to 1 N acids in a perchlorate medium, while it increases significantly in a sulfate medium (Fig. 5); it is ~ 0.06 V higher in 1 N H_2SO_4 than in 1 N $HClO_4$. This latter fact is in agreement with the data of Kashcheev [31] who found while recording anodic polarization curves along the forward path that E_p was 0.1 V higher in 1 N H_2SO_4 than in 1 N $HClO_4$. Since the 1 N $HClO_4$ solution is more acidic than the 1 N H_2SO_4 solution, this means that even in solutions with rather high H^+-ion activities, the potential for iron passivation is governed not by the pH, but by the anion composition (a qualitatively similar effect was shown for stainless steel in $HClO_4$ + HCl solutions by Trabanelli and Zucchi [32].

This effect is apparently associated with the circumstance that, in going from a weakly acid solution to a very acid solution, the anion composition in a perchlorate medium remains the same, while that in a sulfate medium changes, because the HSO_4^- ions become dominant, instead of the SO_4^{2-} ions. According to data [33] and a calculation [34], the SO_4^{2-} activity in 1 N H_2SO_4 should become extremely small, both in absolute value and in comparison with the activity of HSO_4^- ions. Taking Eq. (7) into account, one can explain the increased passivation potential in the transition from 1 N Na_2SO_4 to 1 N H_2SO_4 by the sharp drop in the SO_4^{2-} ion activity.

It follows from the above that one should not measure the iron passivation potential without maintaining the solution anion composition at a constant value. Indeed, by arbitrarily varying the anion composition, one can obtain a multitude of fictitious pH "dependences" of the passivation potential.

CONCLUSIONS

We have shown the different dependences of the iron passivation potential on the solution composition in nitrate, acetate, and borate solutions on the one hand, and in sulfate and perchlorate solutions on the other. In the first case, the passivation potential is greatly lowered with increased pH, and depends comparatively slightly on the anion composition of the solution, while in the second case it is independent of the pH, and is governed by the nature and concentration of the anion, and apparently the activity of the water.

It has been suggested that in the first case an oxide (or oxygen) passivating layer forms preferentially in a direct reaction of iron with water, while in the second case anions participate in and accelerate the reaction.

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