CHARACTERISTICS OF IRON PASSIVATION IN SULFATE SOLUTIONS

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Many authors have concluded (primarily when working with acid solutions) that iron passivation takes place at a certain potential which depends only on the medium's acidity. In [1-3], we showed that in neutral solutions of Na_2SO_4 two passivation potentials are observed on the anode polarization curve of iron (Fig. 1, curve 1). The first of these (E_1, curve 1) is independent of the content of Na_2SO_4 and a number of other salts in the solution and, as stated in [4], is shifted to the negative side with increasing pH.

In a certain range of potentials more positive than E_1 on the sector ab of curve 1 passive iron is activated by SO_4'' ions. However, with a further shift in potential towards the positive side, activation is suppressed (sector cd) and iron goes over to the second passive state (sector de). Owing to the diffuse nature of the 2nd maximum sector bc), it is convenient to take as the second passivation potential that of the boundary of the second passivation range (E_2, curve 1).

In [5] we showed that in solutions with constant concentration of SO_4'' ions (0.5 g-ion/liter) E_2 is virtually independent of pH in the pH range 2-8.5. Further measurements established that this independence is retained in pH 12 (Fig. 2, 1). During determination of the reverse curves, activation of the electrode was not observed at pH 12.4. This was evidently due to the fact that iron activation by SO_4'' ions in the 1st passive range is retarded with increasing pH [1]: at sufficiently high concentrations of OH' ions, the second loop on the polarization curve (abcd on curve 1, Fig. 1) should disappear (like the first loop [6]).

From these data we can infer that between pH 2 and 12

$$\partial E_2 / \partial pH = 0. \quad (1)$$

Equation (1) cannot be explained by the formation of a layer of solution near the electrode with constant acidity despite changes in the solution pH, because there is close agreement between the results of measurements in buffer and non-buffer solutions (Fig. 2), and, in addition, intensive stirring of the solution was found to have no effect on the value of E_2. Thus, the solution pH actually has no effect on the second passivation potential.

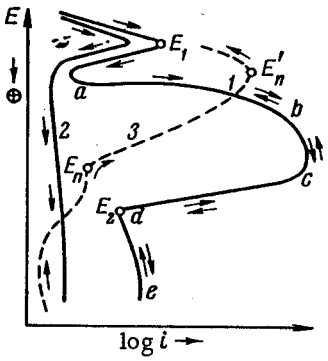

Fig. 1. Schematic anode polarization curves of iron: 1) in neutral 1 N $NaSO_4$; 2) in neutral base electrolyte (without Na_2SO_4); 3) in weakly acid 1 N $NaNO_3$. The arrows indicate the directions of potential shift during curve determination.

This conclusion is clearly illustrated by data for $CdSO_4$ solutions, of which the acidities increase markedly with increasing salt concentration, owing to intense hydrolysis. Plotting E_2 versus solution pH, we get a paradoxical result, namely, an increase in passivation potential with increasing pH (Fig. 3, 1). In point of fact, control experiments (curves 2, 3) showed that at constant SO_4'' concentration E_2 is independent of pH, as in the case of Na_2SO_4 solutions. Naturally, the ratio reflected by curve 1 has no real existence and is given merely as a convincing example of the inapplicability of certain general passivation laws to the 2nd iron passivation in sulfate solutions. On the other hand, these data indicate the unreliability (even absurdity) which may result when passivation potentials are measured without keeping the anionic composition of the solution constant.

It will be seen from Fig. 4 that in Na_2SO_4 (curves 1, 1') and $CdSO_4$ (curve 2) solutions, E_2 is shifted to the positive side with increasing sulfate concentration; in this connection the value of E_2 is not affected by the method of performing the experiment (i.e., it makes no difference whether the salt concentration changes with constant or variable pH). There is a marked difference between curves (1, 1') and 2 of Fig. 4; to explain this we

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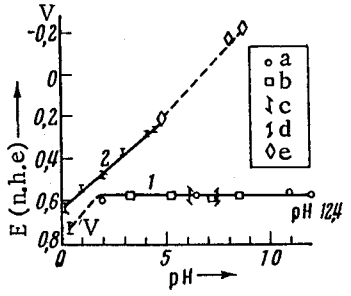

Fig. 2. 1) Second passivation potential versus pH in solutions containing 0.5 g-ion liter SO_4''; a and b) data for Fe-TsNIIChM in nonbuffer and buffer solutions of Na_2SO_4 respectively; c and d) data for Armco iron and Hilger iron respectively, obtained during determination of the forward polarization curves and by the potential drop method. 2) E_p versus pH in solutions with 1 g-ion/liter NO_3' ($NaNO_3 + HNO_3$); e) data for E_p (from [17] in 5 N NH_4NO_3.

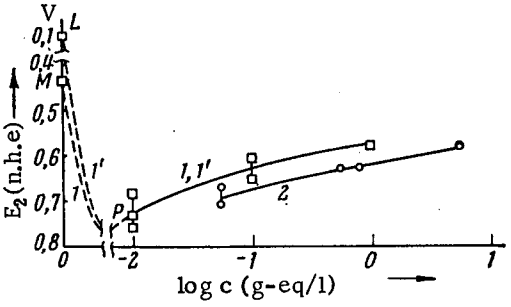

Fig. 4. Second passivation potential versus Na_2SO_4 concentration at pH 3.3(1) and pH 5.3(1') and versus $CdSO_4$ concentration (2). Points L and M correspond to the passivation potentials in base electrolytes containing buffers (sodium tetraborate + succinic acid); point P corresponds to the most probable value of E_2 in 0.01 N Na_2SO_4.

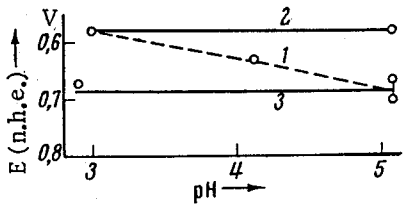

Fig. 3. Second passivation potential plotted versus pH in $CdSO_4$ solutions. 1) pH increases owing to falling $CdSO_4$ concentration in the solution; 2 and 3) SO_4'' concentration constant (2.84 and 0.0284 g-ion/liter respectively).

cannot exclude completely the possibility that the nature of the salt cations has an influence (because the authors of [7] have shown that Cd^{+2} ions are strongly adsorbed on a Pt electrode at positive potentials). However, in this connection the decisive role will be played by the difference between the activity coefficients of Na_2SO_4 and $CdSO_4$ (when E_2 is plotted versus salt activity* the data for both sulfates lie on the same straight line). Its equation is as follows:

$$E_2\,(\text{V}) = 0.51 - 0.03 \log a. \qquad (2)$$

Here a is the activity of the salt, and the constant (0.51 V) is found by extrapolation of the 2nd passivation potential at a sulfate activity equal to 1. Owing to the marked scatter of the data for solutions with low sulfate activities, the accuracy of (2) is low; furthermore, from (2) we cannot plot E_2 versus SO_4'' activity, which is the relation of maximum theoretical interest.† However, (2) may be considered as suitable for practical purposes.

It is very difficult to explain our results, particularly the transition of SO_4'' ions from activating to passivating particles (in sector bc of curve 1, Fig. 1), on the basis of passivation theory (i.e., passivation by direct deposition of oxygen on the surface)‡. The following assumptions may be taken as working hypotheses for subsequent investigations: under these conditions, with increasing potential the relation between the adsorbed SO_4'' ions and iron changes in such a way that they either form a passivating layer or begin to transfer oxygen from the water molecules to the metal. In the latter case the first stage of the process may be oxidation of Fe with reduction of SO_4'' ions to a compound of sulfur with valence less than +6 (e.g., SO_2), and the second stage rapid anodic oxidation of this compound by water to SO_4''. Fischer [13] has presented this hypothesis in a different form.

However, at present we can affirm only that, in the case of E_2, Eqs. (1) and (2) exclude the explanation (frequently employed in the phase theory of passivity) of the passivation potential as the values corresponding to equilibrium reaction of a metal-oxide or oxide electrode (e.g., of the type $nMe + mH_2O = Me_nO_m + 2mH^+ + 2me$ or $Me_nO_m + lH_2O = Me_nO_m + l + 2lH^+ + 2le$).

*The data required for calculating the activities were taken from [8].

†It is known [9] that appropriate processing of the results is only possible if we make theoretical assumptions which cannot be checked experimentally.

‡The change in the role of the OH' ion during solution with increasing potential, which occurs in certain systems, may be considered (formally, at least) as an analogous transition. For example, in the case of Ni these ions accelerate solution in the active range [10], but facilitate transition to the passive state [11]. This effect must also occur during solution of iron in dilute alkalis [12].

Our results should be compared with data on iron passivation in 1 N H_2SO_4, which has been studied by many authors. It will be seen from Fig. 2 (point B) that in this medium the passivation potential, determined by the same method as for E_2 in sulfate solutions, has a more positive value (0.7-0.75 V, which agrees with [14]). This displacement is too great to be explained merely by a fall in SO_4'' ionic concentration (according to Young and Blatz [15], in 1 N H_2SO_4 the ratio HSO_4' : SO_4'' is 3:1). However, if we assume that this displacement is due to a fall in pH, and start with the above reactions for a metal-oxide electrode, it is difficult to understand the results of Hines and Williamson [16]; according to these authors, in 60-96% H_2SO_4 solutions (i.e., at an acid acidity 2-3 orders of magnitude higher, and a water activity 1-2 orders of magnitude lower than in 1 N H_2SO_4), passivation takes place at virtually the same potential as in 1 N acid.

In contrast to these data for sulfate solutions, E_p, the passivation potential of iron in solutions with 1 g-ion /liter NO_3', is displaced regularly to the negative side with increasing pH (curve 2, Fig. 2). In this connection the shape of the polarization (curve 3, Fig. 1) at pH > 2 is the same as that of the "forward" polarization curve in 5 N NH_4NO_4 at pH 4.8, obtained by Mieluch [17], and, in the case of 1 N $NaNO_3$ with pH 4.5, E_p', the potential corresponding to the current maximum, is practically the same as the value calculated from the empirical equation [17] for 5 N solutions of NH_4NO_3 : $E_p' = 0.18-0.06$ pH. Therefore, in general we must not exclude the possibility of equilibrium reactions of the metal-oxide electrode in the case of iron passivation in nitrate solutions. It should be mentioned that, in contrast to SO_4'' ions, under our experimental conditions addition of NO_3' ions did not lead to the appearance of a second current maximum on the polarization curve [1]. On the other hand, judging from preliminary data, in the case of solutions of sodium perchlorate (of which the addition at pH 7.4 leads to the appearance of a second current maximum on the polarization curve [18]), the value of E_2 in weakly acid solutions is independent of pH, but, as in sulfate solutions, depends on the anionic concentration.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of the first issue of this year.