CLARIFICATION OF THE KINETIC PARAMETERS OF THE REACTION OF THE ACTIVE DISSOLUTION OF IRON IN PHOSPHATE SOLUTIONS

A. N. Katrevich, G. M. Florianovich, and Ya. M. Kolotyrkin

UDC 620.193.01

A study was made of the dependence of the rate of dissolution of iron in the passive state in phosphate media with intense mixing (without the formation of protective layers of difficultly soluble salts) on the acidity of the solution and on its phosphate content. It is established that the rate of dissolution at a pH from 0.75 to 4.0 rises with a rise in the pH in accordance with a first-order relationship and does not depend on the phosphate concentration, while, with a pH from 4.0 to 7.0, the rate does not depend on the acidity and rises by one order of magnitude with a ten-fold increase in the concentration of $H_2PO_4^-$ ions. A conclusion is drawn with respect to the change in the mechanism of the dissolution of iron with a transition from solutions with a pH < 4.0 to solutions with a pH > 4.0. Reaction schemes are proposed for both mechanisms.

Elucidation of the mechanism of the electrochemical dissolution of iron in phosphate solutions is rendered difficult by the concomitant covering of its surface by difficultly soluble salts which is observed at values of the pH > 4 [1], but which can be avoided under intense mixing conditions (for example, with a rate of rotation of a disc-shaped electrode at a rate of 2700 rpm or greater [1]).

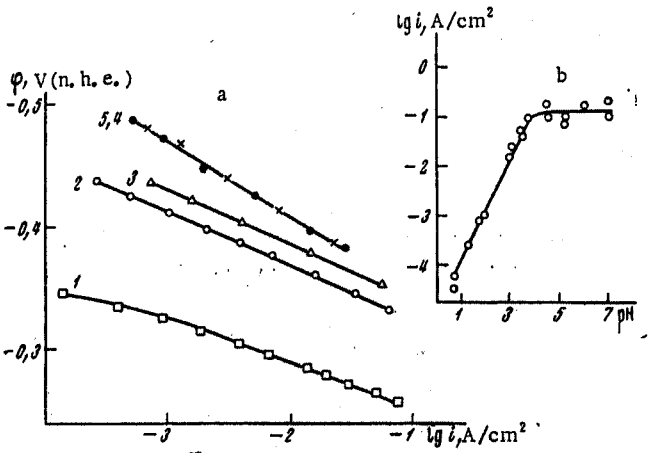

Fig. 1. Data from polarization measurements for iron in a 0.165 M phosphate solution: a) anode polarization curves with pH; 1) 1.2; 2) 3.1; 3) 3.5; 4) 4.5; 5) 6.0; b) dependence of anode current on the potential with a potential of −0.35 V.

L. Ya. Karpov Physicochemical Scientific Research Institute. Translated from Zashchita Metallov, Vol. 10, No. 4, pp. 369-373, July-August, 1974. Original article submitted August 4, 1972.

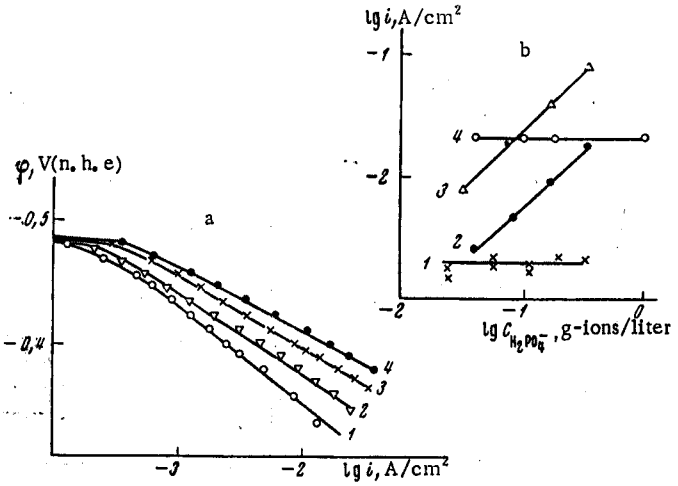

Fig. 2. a) Anode polarization curves for iron at pH 5.2 and different concentrations of phosphate (M): 1) 0.04; 2) 0.08; 3) 0.165; 4) 0.33; b) dependence of anode current with a constant potential on the concentration of $H_2PO_4^-$ anions, C_1, under the conditions: 1) pH 1.7, $\varphi = -0.33$ V; 2) pH 5.2, $\varphi = -0.40$ V; 3) pH 4.5, $\varphi = 0.37$ V; 4) pH 3.5, $\varphi = -0.36$ V.

Data on the electrochemical behavior of iron in neutral and weakly acidic phosphate solutions with controlled mixing are very limited. With a rate of rotation of the disc equal to 2000 rpm and a pH of 5.9, a first-order reaction with respect to $H_2PO_4^-$ ions is found [2]. An analogous result was obtained in [3] with pH $\geq$ 3.3; here it was shown that, with a pH from 2.0 to 3.3, dissolution of iron is accelerated with a rise in the pH.

The present authors made a study of the effect of the phosphate concentration (from 0.01 to 2.5 M) and of the pH of the solution (from 0.75 to 7.0) on the rate of dissolution of an iron disc-shaped electrode in the region of potentials preceded by primary passivation. The method used for preparing the solutions and the electrodes, as well the measurement method, are set forth in [1]. The rate of rotation of the disc was 2780 rpm, and the rate of change of the potential was 100 mV/h. The potentials were given with reference to a normal hydrogen electrode.

In acid phosphate solutions (pH < 4), there is observed the linear rise of the logarithm of the rate of the anodic dissolution of iron with an increase in the pH (Fig. 1) which is well known [4] for solutions with other anions. With a pH > 4, such a dependence is not present.

A value of the pH equal to 4 is a critical value also from the point of view of the effect of the phosphate concentration. With a pH < 4, the introduction of and the subsequent increase in the content of phosphate at a constant value of the pH has no effect whatsoever on the rate of the process. However, the rate of the process rises sharply with an increase of the phosphate concentration with a pH > 4; under these circumstances, the corrosion potential practically does not change (Fig. 2a). The dependence of log i with φ = const on the logarithm of the total phosphate concentration, found from the data of Fig. 2a, is linear, with a slope close to unity.

Phosphate solutions in the pH region under investigation may have in their composition phosphate ions of different nature: $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-}. To judge which of these ions participate in the process we calculated the concentrations of $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-} ions (respectively, C_1, C_2, and C_3), as well as the concentration of H_3PO_4 molecules (C_4) with a constant total phosphate concentration, C_{ph}, and different concentrations of H^+ ions (C_H). The calculation was made using the formulas

$$C_1 = \frac{C_{ph} K_1 C_H^2}{K_1 K_2 K_3 + K_1 K_2 C_H + K_1 C_H^2 + C_H^3},$$

$$C_2 = \frac{C_{ph} K_1 K_2 C_H}{K_1 K_2 K_3 + K_1 K_2 C_H + K_1 C_H^2 + C_H^3},$$

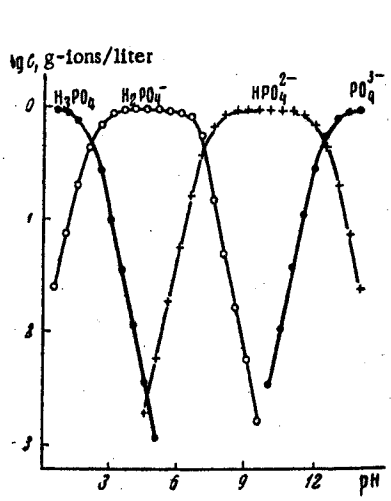

Fig. 3

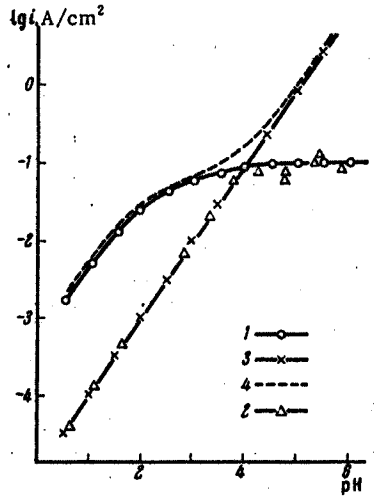

Fig. 4

Fig. 3. Dependence of concentrations of H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-} on the pH of the solution, with a total phosphate content of 1 M.

Fig. 4. Comparison between the experimental dependence of the rate of dissolution of iron on the pH for a 0.165 M phosphate solution at a potential of −0.35 V (curve 2) and the results of corresponding calculations using formulas (1, 3, and 4) (curves 1, 3, and 4).

$$C_3 = \frac{C_{ph} K_1 K_2 K_3}{K_1 K_2 K_3 + K_1 K_2 C_H + K_1 C_H^2 + C_H^3}$$

$$C_4 = C_{ph} - C_1 - C_2 - C_3,$$

where K_1, K_2, and K_3 are the dissociation constants for phosphoric acid, equal, respectively, to $7.52 \cdot 10^{-3}$, $6.3 \cdot 10^{-8}$, and $1.26 \cdot 10^{-12}$ [5]. The results of this calculation, which are in agreement with [6], are given on Fig. 3 for a total concentration of phosphate equal to 1 M. As can be seen, with a pH from 4 to 7, $H_2PO_4^-$ ions are present in the greatest concentration. For the HPO_4^{2-} ion at these values of the pH, there is observed a strong increase in the concentration with a rise in the pH. If only these ions took part in the reaction, there would be anticipated a dependence of the reaction rate not only on the total phosphate concentration, but also on the pH of the solution. The absence of such a dependence (on the pH) indicates that, with pH > 4, the process of dissolution takes place without the participation of HPO_4^{2-} ions.

The concentration of $H_2PO_4^-$ ions in the pH region 4-7, on the contrary, is practically constant (Fig. 3); consequently, it can vary only as the result of a change in the phosphate content in the solution. Therefore, out of all the phosphate ions, the most probable participant in the reaction in the given pH region is precisely this ion, which permits the experimental data on the dependence of log i on log C_{ph} in the form of a dependence of log i on log C_1. The latter has already been found to be linear, with a slope close to unity (Fig. 2b).*

As follows from the data obtained, in the region pH < 4, the process of the dissolution of iron takes place with the participation of OH^- ions. The above-noted absence of an effect of C_{ph} shows that, in contrast to sulfate ions [7], phosphate ions do not participate in this process; therefore, the rate of the process, i_1, can be described by the equation [4]

$$i_1 = K_1 C_H^{-1} \exp\left[(1+\beta_1)\varphi F/RT\right]. \quad (1)$$

*Since with a pH < 3 the concentration of $H_2PO_4^-$ ions depends strongly on the pH (Fig. 3), it can be postulated that the dependence of the rate of dissolution on the acidity of the solution, observed in this pH region, is also connected with the participation of $H_2PO_4^-$ ions in the process. However, such a conclusion is not in agreement with the absence of a dependence of the rate of the process on the phosphate concentration with a constant pH.

With pH > 4, the process takes place with the participation of $H_2PO_4^-$. Taking account of the inclination (60 mV), for this pH region the following dissolution mechanism can be postulated:

$$Fe+H_2PO_4^- \rightarrow (FeH_2PO_4)^+ + 2e,$$
$$(FeH_2PO_4)^+ \rightleftharpoons Fe^{2+} + H_2PO_4^- \quad (2)$$

with the slow stage (2). Under this assumption, the reaction rate is described by the equation

$$i_2 = K_2 C_1 \exp(2\beta_2 \varphi F/RT). \quad (3)$$

The experimental results cannot be explained by the simultaneous parallel course of dissolution reactions of iron in accordance with the mechanisms discussed above, with the predominance of one of them (depending on the ratio of the concentrations of the participants in the reaction, i.e., OH^- ions and $H_2PO_4^-$ ions). In fact, if, with a given composition of the solution, the measured current, i_a, is the sum of the currents i_1 and i_2, described, respectively, by Eqs. (1) and (3), the following relationship must be satisfied

$$i_a = i_1 + i_2 = K_1 C_H^{-1} \exp[(1+\beta_1)\varphi F/RT] + K_2 C_1 \exp(2\beta_2 \varphi F/RT). \quad (4)$$

The constant K_2 can be found from the experimental dependence of the current on C_1 with pH > 4, and the constant K_1 from the dependence between the current and the pH with pH < 4. The dependence of the current on the pH for a solution with a total phosphate concentration equal to 0.165 M, calculated using Eq. (4), taking account of the values found for K_1 and K_2, diverges strongly from the experimental curve (Fig. 4), which actually excludes the possibility of the above explanation.

The change in the mechanism of the dissolution when the above-mentioned critical value of the pH (~4) is exceeded can be connected with an increase in the adsorption of $H_2PO_4^-$ ions in the region of active dissolution potentials with a rise in the pH [8, 9] and the associated (due to competing adsorption) lowering of the covering of the surface of the electrode by OH^- ions with the dissociative adsorption of molecules of water.

LITERATURE CITED

1. A. N. Katrevich, Ya. M. Kolotyrkin, and G. M. Florianovich, Zashchita Metal., 10, 239 (1974).
2. Ya. M. Kolotyrkin, Yu. A. Popov, Yu. V. Alekseev, G. M. Florianovich, M. D. Kononova, K. A. Mishenina, and G. M. Ostrovskii, Élektrokhimiya, 8, No. 3 (1972).
3. V. M. Kirnos and A. Ya. Shatalov, Summary of Paper Delivered at the VI Perm' Conference on the Protection of Metals from Corrosion, Perm' (1970), p. 29; Summary of Paper Delivered at an All-Union Conference on Electrochemistry, Tbilisi (1969), p. 706.
4. G. M. Florianovich, L. A. Sokolova, and Ya. M. Kolotyrkin, Élektrokhimiya, 3, 1027 (1967).
5. Chemist's Handbook [in Russian], Izd. Khimiya, Vol. 3 (1965), p. 80.
6. M. S. Pasechnik, T. A. Tumanova, I. A. Volodina, and L. V. Dubravitskaya, Vestnik LGU Ser. Fiz. i Khim., 22, 159 (1966).
7. G. M. Florianovich, L. A. Sokolova, and Ya. M. Kolotyrkin, Élektrokhimiya, 3, 1359 (1967).
8. L. Formaro and S. Trasatti, Electrochim. Acta, 15, 729 (1970).
9. J. G. N. Thomas, Brit. Corros. J., 1, 156 (1966); 2, 13 (1967).