Cyclic voltammetric study of the $HCl–H_3PO_4–H_2O–Fe(III)$ system

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Abstract

The electrochemical behavior of Fe(III) cations on a platinum electrode in the $HCl–H_3PO_4–H_2O$, $HCl–H_2O$, $H_3PO_4–H_2O$ systems (25–95°C) has been studied by cyclic voltammetry. The oxidizing ability of the 2.0 M $HCl+H_3PO_4$ system containing 0.10 M Fe(III) decreases as the molar fraction of H_3PO_4 increases. The observed effect results from the formation of Fe(III) complexes with phosphate anions that are weaker oxidants than the corresponding hydrate and chloride complexes. An increase in temperature causes an increase in the oxidizing ability of the $HCl–H_3PO_4–H_2O–Fe(III)$ system. Addition of H_3PO_4 to HCl solutions converts Fe(III) cations from hydrate and chloride complexes to phosphate complexes, which leads to a decrease in their diffusion rate in aqueous acid solutions. The decrease in the diffusion coefficient of Fe(III) cations in 1.0 M HCl+1.0 M H_3PO_4 is about 70% of the initial value. A probable reason for more efficient protection of low-carbon steel by triazole-based composite inhibitors in H_3PO_4 or its mixtures with HCl containing Fe(III), in comparison with similar solutions of HCl alone, is that phosphate complexes of Fe(III) are formed in these media. They have a lower oxidizing ability and diffusion rate in comparison with aqueous and chloride complexes of Fe(III).

Keywords: *corrosion inhibitors, cyclic voltammetry, hydrochloric acid, phosphoric acid, Fe(III)/Fe(II) redox couple, diffusion coefficient.*

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Introduction

Etching of steels in solutions of hydrochloric acid is accompanied by accumulation of Fe(III) chloride due to dissolution of scale and oxidation of Fe(II) salts that are formed in the reactions of scale and metal with the acid with atmospheric oxygen [1, 2]. The dissolution of steels in acid solutions containing Fe(III) chloride occurs not only due to the reaction of iron with an acid:

$$Fe + 2HCl = FeCl_2 + H_2,$$

but also due to the parallel reaction of the metal with a Fe(III) salt:

$$Fe + 2FeCl_3 = 3FeCl_2.$$

Fe(III) chloride can considerably decrease the protective effect of metal corrosion inhibitors added to an etching solution [3].

The adverse effect of Fe(III) chloride on the protective effect of corrosion inhibitors toward mild steels can be overcome by replacing hydrochloric acid solutions with HCl + H_3PO_4 mixtures containing a formulation of IFKhAN-92 (a 1,2,4-triazole derivative), KNCS and urotropine with a 9:1:400 molar ratio of the components. Such inhibited solutions are resistant against the accumulation of Fe(III) salts at HCl concentrations up to 60% of the total amount of acids in a solution [4].

Previously, the potentiometry method was used to study an $HCl–H_3PO_4–H_2O$ system containing Fe(III) and Fe(II) cations [5]. It was shown that a probable reason of the efficient protection of mild steel by triazole-based composite inhibitors in H_3PO_4 or its mixtures with HCl containing Fe(III), in comparison with similar solutions of HCl alone, is that phosphate complexes of Fe(III) are formed in these media. They have lower oxidizing ability in comparison with aqueous and chloride Fe(III) complexes.

To reach a more detailed understanding of the processes that occur in the $HCl–H_3PO_4–H_2O$–Fe(III) system and to identify the role of H_3PO_4 additives in preserving the protective action of the triazole-based composite inhibitor of in the presence of Fe(III) salts, it seems necessary to study these solutions by the cyclic voltammetry method (CVA). This method is used quite successfully to study solutions containing Fe(III) and Fe(II) cations alone or their mixtures [6–15]. The effect of additives H_3PO_4 on the characteristics of the Fe(III)/Fe(II) redox process in H_2SO_4 solutions was studied by CVA [6]. Addition of phosphoric acid reduces the redox potential of the Fe(III)/Fe(II) couple ($E_{\mathrm{Fe(III)/Fe(II)}}$) in this medium. The observed effects result from the binding of Fe cations into phosphate complexes that are characterized by higher stability compared to iron hydrate and sulfate complexes. This complexes have a lower oxidizing ability and diffusion rate in comparison with aqueous and sulfate complexes of Fe(III). The decrease in the diffusion coefficient of Fe(III) cations is about 1/3 of the initial value.

Experimental

Solutions were prepared from HCl and H_3PO_4 of "chemically pure" grade and distilled water. H_3PO_4 solution containing Fe(III) salts were obtained by dissolving $Fe(OH)_3$ precipitated with NaOH ("chemically pure" grade) from a $FeCl_3$ solution, in excess H_3PO_4. The Fe(III) chloride solutions was prepared from $FeCl_3 \cdot 6H_2O$ ("pure" grade).

CVA studies were performed using an EL-02.061 potentiostat in a thermostated three-electrode glass cell with divided electrode spaces. A platinum wire (area (S) 15.9 mm^2) served as the working electrode. A silver chloride electrode was used as the reference electrode, and a platinum plate ($S = 1.5$ cm^2) was used as the auxiliary electrode. Potential scanning was performed from 1.4 V to 0.0 V, and then from 0.0 V to 1.4 V. The scan rates were 0.02, 0.05, 0.10, 0.20 and 0.40 $V \cdot s^{-1}$. The solutions studied were deaerated with argon both before (for 30 min) and during an experiment. Before an experiment, the working electrode was degreased with acetone, kept for 3 min in concentrated HNO_3, and washed with distilled water. The temperature (t) range of the studied solutions was 25–95°C. The accuracy of temperature control was ±1°C. Electrode potentials are reported *versus* the standard hydrogen electrode.

Experimental results and discussion

The cyclic voltammograms of a Pt electrode in 2.0 M HCl + 0.10 M $FeCl_3$ at 25°C (Figure 1, Table 1) contain two peaks, the maxima of which are located at $E = 0.63–0.64$ V and 0.71–0.73 V, depending on the potential sweep rate (v). The first cathodic peak corresponds to the reduction of Fe(III) cations on the Pt electrode:

$$Fe^{3+} + e^{-} = Fe^{2+},$$

The second peak, *i.e.*, the anodic one, corresponds to the oxidation of the Fe(II) cations formed:

$$Fe^{2+} - e^{-} = Fe^{3+}.$$

As v increases, the maximum potential of the cathodic peak (E_{pc}) virtually unchanged, while the anodic peak (E_{pa}) weakly grows. The currents in the cathodic and anodic peak maxima (I_{pc} and I_{pa}) increase with increasing v and $I_{pa}/I_{pc} = 1$. The system under study is quasi-equilibrium since the criterion for equilibrium systems is not satisfied for it: $E_{pa}–E_{pc} > 0.057$ V, but both peaks, the cathodic and anodic ones, are present on the voltammograms [16]. The half-wave potential:

$$E_{1/2} = \frac{E_{pc} + E_{pa}}{2},$$

which is often interpreted as the redox potential of a system, does not depend on v within the measurement accuracy limits. A decrease in the content of Fe(III) in the acid solution does not significantly change the nature of cyclic voltammograms (Figure 2, Table 1), but the values of I_{pc} and I_{pa} decrease.

The values of current maxima on the current-potential curves is determined by the Randles–Sevcik equation:

$$I_p = 2.69 \cdot 10^5 z^{1.5} S C D^{0.5} v^{0.5},$$

where $2.69 \cdot 10^5$ is the equation constant at 25°C; z is the number of electrons participating in the redox process ($z = 1$ for the redox pair Fe(III)/Fe(II)); S is the surface area of the electrode (m^2); C is the concentration of the electrochemically active substance ($mol \cdot m^{-3}$); D is the diffusion coefficient ($m^2 \cdot s^{-1}$); and v is the potential sweep rate ($V \cdot s^{-1}$). The Randles–Sevcik equation describes redox processes that occur in equilibrium systems. However, it is noted that it can be used to describe quasi-reversible and even irreversible systems [16]. The criterion for the applicability of this equation for describing the cathode process in this system is that the I_{pc} *vs.* $v^{0.5}$ (Figure 3) and I_{pc} *vs.* $C_{Fe(III)}$ plots (Figure 4) should be linear.

Table 1. CVA data of platinum electrode in 2.0 M HCl + $FeCl_3$ at 25°C.

Scan rate (v), $V \cdot s^{-1}$	**Cathodic peak potential (E_{pc}), V**	**Anodic peak potential (E_{pa}), V**	**Peak potential separation ($E_{pa}-E_{pc}$), V**	**Half-wave potential ($E_{1/2}$), V**	**Cathodic peak current (I_{pc}), mA**	**Anodic peak current (I_{pa}), mA**	**Peak current ratio (I_{pa}/I_{pc})**
0.01 M $FeCl_3$							
0.10	0.64	0.71	0.07	0.68	0.27	0.27	1.00
0.04 M $FeCl_3$							
0.10	0.64	0.72	0.08	0.68	1.3	1.3	1.00
0.10 M $FeCl_3$							
0.02	0.64	0.71	0.07	0.68	1.4	1.4	1.00
0.05	0.64	0.72	0.08	0.68	2.2	2.2	1.00
0.10	0.64	0.72	0.08	0.68	3.2	3.2	1.00
0.20	0.64	0.73	0.09	0.69	4.4	4.4	1.00
0.40	0.63	0.73	0.10	0.68	6.2	6.2	1.00

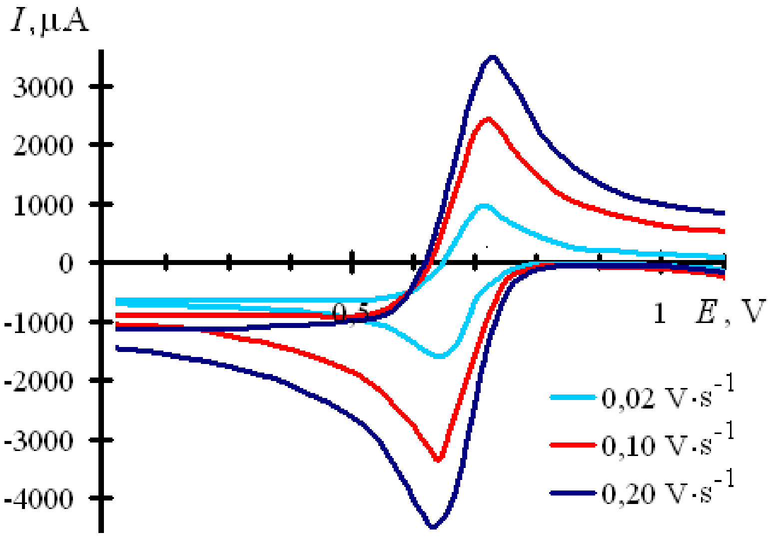

Figure 1. Cyclic voltammograms of platinum electrode in 2.0 M HCl + 0.10 M $FeCl_3$ at different scan rates at 25°C.

The peaks on the voltammograms of a Pt electrode in HCl + H_3PO_4 solutions containing 0.10 M Fe(III) are shifted towards lower potentials in comparison with the solution of HCl alone, and are characterized by higher non-equilibrium (Figure 5, Table 2). At 25°C, $E_{pa}-E_{pc} = 0.10–0.25$ V in HCl + H_3PO_4 but as small as 0.08 V in 2.0 M HCl. Already at 10% H_3PO_4 in the solution, the cathodic current decreases. As the content of H_3PO_4 in the mixture increases, the value of $E_{1/2}$ decreases systematically, indicating a decrease in the oxidative capability of the system. The lowest value $E_{1/2} = 0.41$ V is observed in 2.0 M H_3PO_4, against $E_{1/2} = 0.68$ V in 2.0 M HCl.

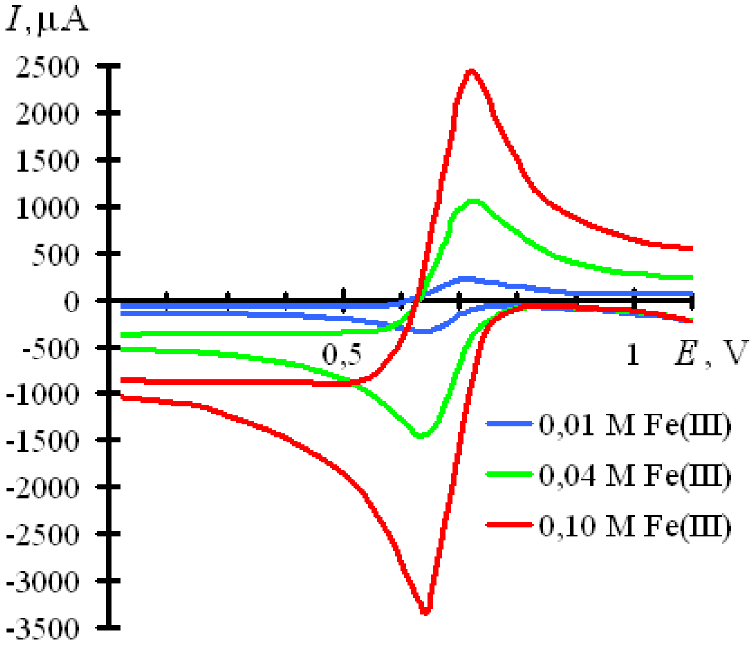

Figure 2. Cyclic voltammograms of platinum electrode in 2.0 M HCl + $FeCl_3$ at different concentration of Fe(III). Scan rate: 0.10 $V \cdot s^{-1}$. $t = 25$°C.

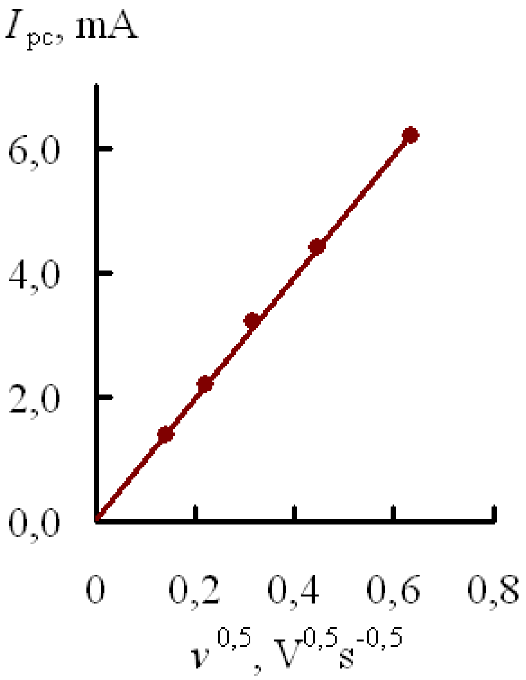

Figure 3. Variation of the cathodic peak current (I_{pc}) *vs.* the square root of scan rate ($v^{0.5}$) for platinum electrode in 2.0 M HCl + 0.10 M $FeCl_3$. $t = 25$°C.

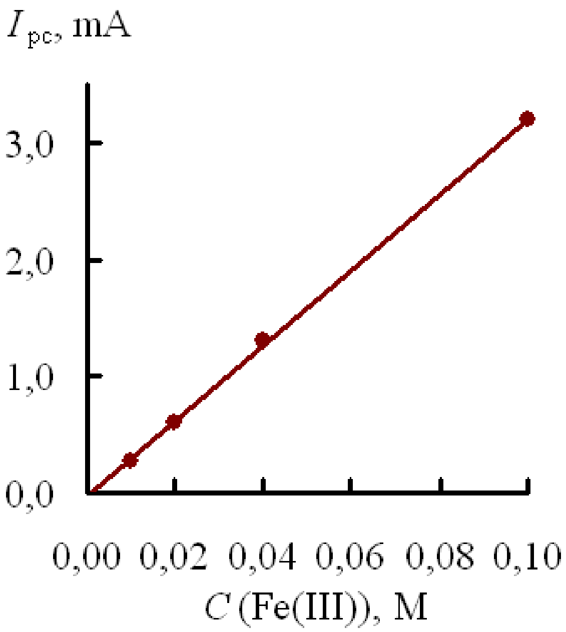

Figure 4. Variation of the cathodic peak current (I_{pc}) *vs*. concentration of $FeCl_3$ for platinum electrode in 2.0 M HCl + $FeCl_3$. Scan rate: 0.10 $V \cdot s^{-1}$. t = 25°C.

Other conditions being equal, an increase in temperature results in an increase in the height of the cathodic and anodic peaks on the voltammograms of acid solutions containing Fe(III) (Figure 6, Table 2). An increase in $E_{1/2}$ is observed. Comparison of the $E_{1/2}$ values obtained from these cyclic voltammograms with $E_{Fe(III)/Fe(II)}$ determined in potentiometric studies [5] shows their good agreement. In 2.0 M HCl + 0.05 M $Fe_2(SO_4)_3$, $E_{1/2} = 0.68–0.72$ V, $E_{Fe(III)/Fe(II)} = 0.67–0.71$ V; in 2.0 M H_3PO_4+0.10 M $FePO_4$, $E_{1/2} = 0.41–0.46$ V, $E_{Fe(III)/Fe(II)} = 0.44–0.46$ V; in 1.0 M HCl+1.0 M H_3PO_4+0.05 M $FeCl_3$+0.05 M $FePO_4$, $E_{1/2} = 0.53–0.63$ V, $E_{Fe(III)/Fe(II)} = 0.56–0.63$ V. These values also agree well in the H_2SO_4+H_3PO_4+H_2O+Fe(III)+Fe(II) system [6, 17]. It should be noted that in [7] larger quantitative differences are observed between the potentials of the Fe(III)/Fe(II) redox pair in H_3PO_4+HF+H_2O Fe(III)+Fe(II) system obtained from the results of parallel measurements by CVA and potentiometry.

It appears important to estimate the effect of H_3PO_4 addition on the diffusion rate of Fe(III) cations in the media being studied. The results that we presented above show the possibility of using the Randles–Sevcik equation for describing the cathodic process in the systems we are studying. The I_{pc} values obtained experimentally allowed us to calculate the $D_{Fe(III)}$ parameter by the Randles–Sevcik equation (Figure 7). The values of the diffusion coefficient of Fe(III) cations show that already at 10% H_3PO_4 in the system, it decreases by about 1/4 compared to the value observed in HCl. The average $D_{Fe(III)}$ value that we obtained in 2.0 M HCl is 540 $\mu m^2 \cdot s^{-1}$, which is close to $D_{Fe(III)} = 470$ $\mu m^2 \cdot s^{-1}$ in 1.0 M HCl according to [18]. The diffusion coefficient of $FeCl_3$ in 2.0 M HCl+0.1 M $FeCl_3$ (25°C) determined by the diaphragm-gel method is 523 $\mu m^2 s^{-1}$ [19].

Table 2. CVA data of platinum electrode in HCl+H_3PO_4+$FeCl_3$+$FePO_4$ system at different temperatures. Scan rate: 0.10 V·s^{-1}.

Temp. (*t*),°C	**Cathodic peak potential (E_{pc}), V**	**Anodic peak potential (E_{pa}), V**	**Peak potential separation (E_{pa}–E_{pc}), V**	**Half-wave potential ($E_{1/2}$), V**	**Cathodic peak current (I_{pc}), mA**	**Anodic peak current (I_{pa}), mA**	**Peak current ratio (I_{pa}/I_{pc})**
2.0 M HCl + 0.10 M $FeCl_3$							
25	0.64	0.72	0.08	0.68	3.2	3.2	1.00
40	0.65	0.73	0.08	0.69	3.8	3.8	1.00
60	0.66	0.74	0.08	0.70	4.4	4.4	1.00
80	0.68	0.75	0.07	0.72	5.2	5.2	1.00
95	0.68	0.76	0.08	0.72	5.6	5.6	1.00
1.8 M HCl + 0.2 M H_3PO_4 + 0.090 M $FeCl_3$ + 0.010 M $FePO_4$							
25	0.60	0.70	0.10	0.65	2.7	2.7	1.00
1.5 M HCl + 0.5 M H_3PO_4 + 0.075 M $FeCl_3$ + 0.025 M $FePO_4$							
25	0.55	0.68	0.13	0.62	2.1	2.3	1.10
1.0 M HCl + 1.0 M H_3PO_4+ 0.050 M $FeCl_3$ + 0.050 M $FePO_4$							
25	0.40	0.65	0.25	0.53	1.7	2.0	1.18
40	0.47	0.65	0.18	0.56	2.2	2.4	1.09
60	0.53	0.66	0.13	0.60	3.0	3.0	1.00
80	0.57	0.66	0.09	0.62	4.1	4.1	1.00
95	0.58	0.67	0.09	0.63	4.7	4.7	1.00
2.0 M H_3PO_4 + 0.10 M $FePO_4$							
25	0.25	0.56	0.31	0.41	1.4	0.99	0.71
40	0.28	0.54	0.26	0.41	1.8	1.4	0.78
60	0.35	0.52	0.17	0.44	2.4	2.3	0.96
80	0.38	0.53	0.15	0.46	3.1	2.9	0.94
95	0.39	0.52	0.13	0.46	3.7	3.3	0.89

The diffusion coefficients of Fe(III) cations in the H_2SO_4–H_3PO_4–H_2O–Fe(III) system were previously obtained [6] (Figure 7). In the HCl–H_3PO_4–H_2O–Fe(III) system, they have higher values. We have shown [3] that the two-component composition (IFKhAN-92+KSCN (9:1)) effectively inhibits the corrosion of low-carbon steel in 1.0 M H_2SO_4+1.0 M H_3PO_4+Fe(III), but this composition weakly slows down corrosion in 1.0 M HCl+1.0 M H_3PO_4+Fe(III). Poor protection of low-carbon steel in this medium can be explained by higher diffusion coefficients of Fe(III). Inhibitory protection of steel more effective in 1.0 M H_2SO_4+1.0 M H_3PO_4, where the diffusion coefficients of Fe(III) cations are lower. These differences are smoothed out using a more complex three-component composition of inhibitors (IFKhAN-92+KSCN+urotropin) [20]. It can be assumed that Fe(III) cations in the presence of urotropine additionally bind into complexes that have weaker oxidizing properties and low diffusion coefficients.

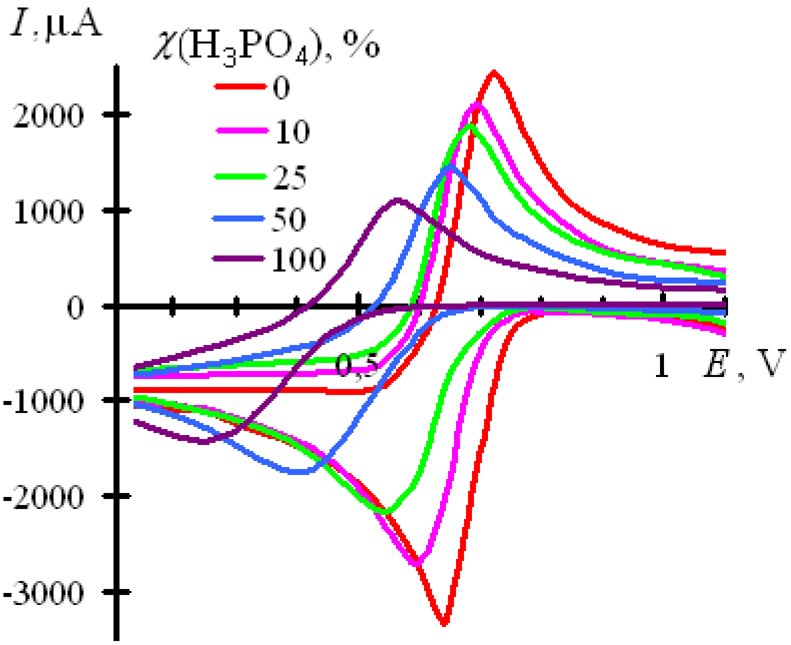

Figure 5. Cyclic voltammograms of platinum electrode in HCl+H_3PO_4+0.10 M Fe(III) (25°C) at different concentration of H_3PO_4. Scan rate: 0.10 $V \cdot s^{-1}$.

Thus, the use of CVA to study HCl+H_3PO_4 mixtures containing Fe(III) allowed us to find additional reasons of the preservation of the protective effect of the IFKhAN-92 based composite inhibitor in the corrosion of steels in these media. Phosphate ions bind the strong oxidant additionally present in the solution, *i.e.*, Fe(III) cations, into strong complexes. These phosphate complexes have lower oxidizing ability and mobility than aqueous and chloride complexes of Fe(III). Addition of H_3PO_4 affects the thermodynamic properties of the corrosive environment by reducing its oxidative capability. This additive also changes the kinetic parameters of the reduction of Fe(III) cations on steel that occurs in diffusion mode [21]. A decrease in the diffusion rate of Fe(III) cations should slow down their reduction. Apparently, such a complex effect should be sufficient to enable the composite inhibitor based on IFKhAN-92 not only to slow down the reduction of protons but also suppress the reduction of Fe(III) cations. At the same time, the IFKhAN-92 inhibitor itself plays an important role in the observed effect. This compound can form monomolecular and polymolecular protective layers on the surface of metals in acid solutions. These layers are strongly bound to the metal surface by chemical bonds [20, 22, 23], which allows the maximum protective effect to be provided in such strongly corrosive environments as acids.

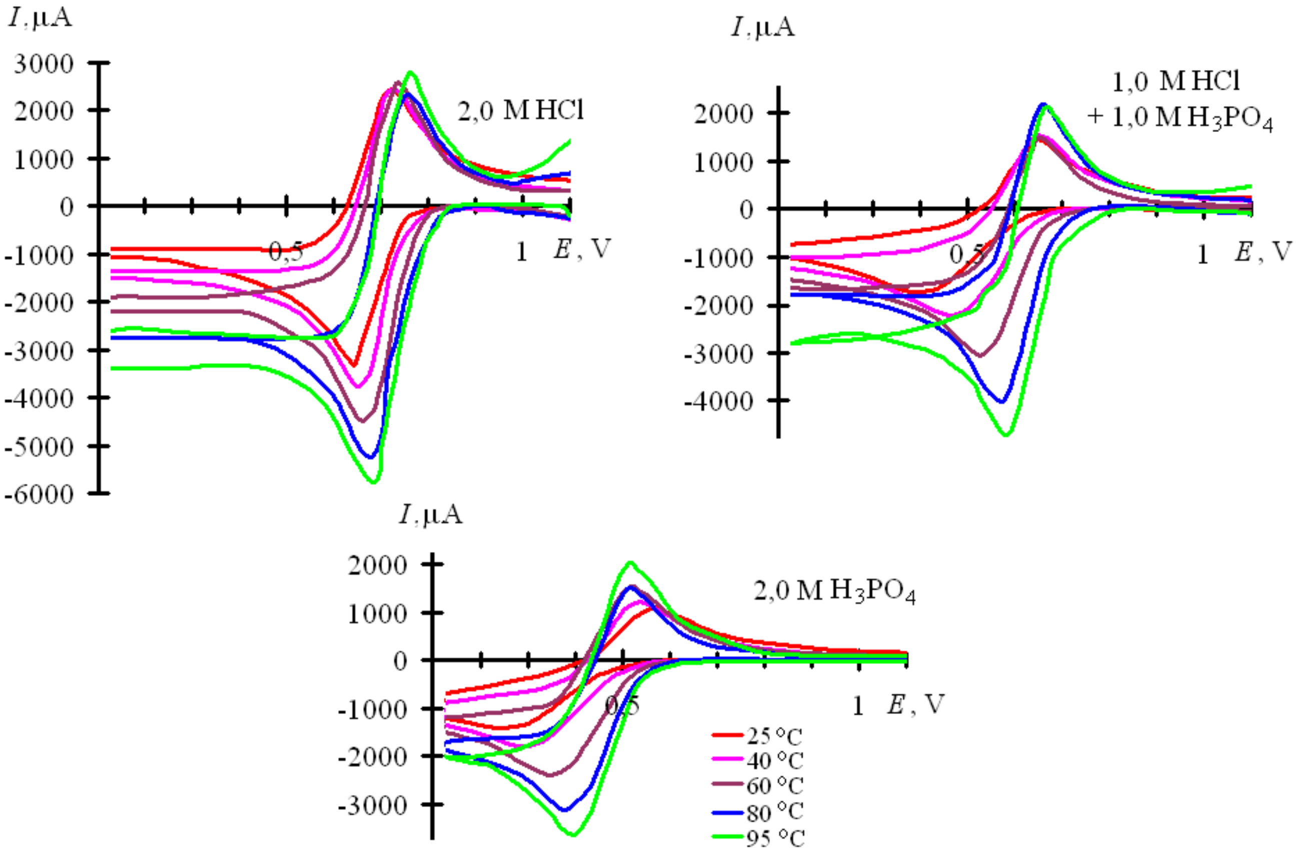

Figure 6. Cyclic voltammograms of platinum electrode in HCl + H_3PO_4 + 0.10 M Fe(III) at different temperatures. Scan rate: 0.10 V·s^{-1}.

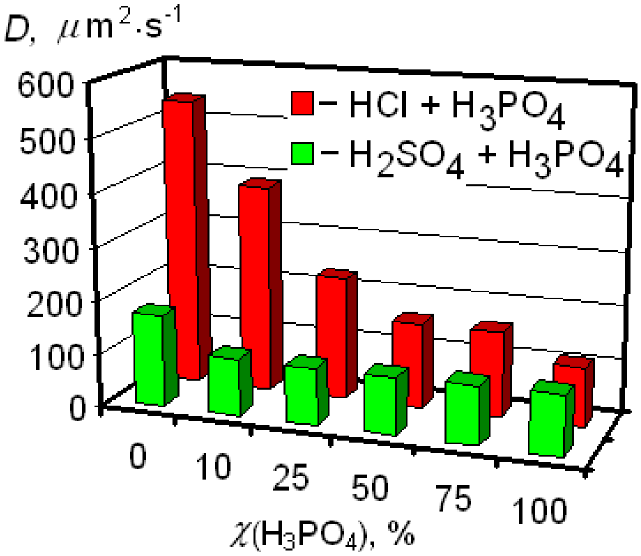

Figure 7. Effect of H_3PO_4 concentration in a HCl + H_3PO_4 + 0.10 M Fe(III) and H_2SO_4 + H_3PO_4 + 0.10 M Fe(III) systems on the diffusion coefficient of the Fe(III) cation. *t* = 25°C.

Conclusions

1. The oxidizing capability of the $HCl–H_3PO_4–H_2O$ system containing Fe(III) decreases as the relative content of H_3PO_4 increases. The observed effect results from the formation of Fe(III) complexes with phosphate anions that are weaker oxidants than the corresponding hydrate and chloride complexes.
2. Addition of H_3PO_4 to HCl solutions converts Fe(III) cations from hydrate and chloride complexes to phosphate complexes, which leads to a decrease in their diffusion rate in aqueous acid solutions. The decrease in the diffusion coefficient of Fe(III) cations in 1.0 M HCl+1.0 M H_3PO_4 is about 70% of the initial value.
3. The oxidizing ability of Fe(III) phosphate complexes is lower than that of its aqueous and chloride complexes. These effects explain the efficient protection of low-carbon steel by composite inhibitors based on triazoles in H_3PO_4 or in its mixtures with HCl containing Fe(III) in comparison with similar solutions of HCl alone.

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