

A potentiometric study of an $\text{H}_2\text{SO}_4\text{--H}_3\text{PO}_4\text{--H}_2\text{O}$ system containing Fe(III) and Fe(II) cations

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Abstract

The potentiometric method was used to study an $\text{H}_2\text{SO}_4\text{--H}_3\text{PO}_4\text{--H}_2\text{O}$ system (20–95°C) containing Fe(III) and Fe(II) cations. The oxidizing ability of the 2 M $\text{H}_2\text{SO}_4 + \text{H}_3\text{PO}_4$ system containing Fe(III) and Fe(II) (1:1) 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 sulfate complexes. Variation in the total content of the equimolar Fe(III) + Fe(II) mixture ($C = 0.01\text{--}0.10$ M) in 1 M $\text{H}_2\text{SO}_4 + 1$ M H_3PO_4 nearly does not affect its oxidizing ability. Conversely, an increase in the relative content of Fe(III) in the system considerably increases its oxidative potential. At a fixed concentration of the Fe(III) + Fe(II) mixture in the system (0.04 M), addition of an equimolar mixture of H_2SO_4 and H_3PO_4 (up to 6 M) somewhat decreases the oxidizing properties of the system.

A probable reason of the efficient protection of low-carbon steel by triazole-based composite inhibitors in H_3PO_4 or its mixtures with H_2SO_4 containing Fe(III), in comparison with similar solutions of H_2SO_4 alone, is that phosphate complexes of Fe(III) are formed in these media. They have lower oxidizing ability in comparison with aqueous and sulfate complexes of Fe(III).

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Introduction

The use of H_2SO_4 process solutions under various industrial conditions often results in the accumulation of Fe(III) sulfate. Corrosion of steel items in these media results not only from the reaction of the metal with the acid but also with $\text{Fe}_2(\text{SO}_4)_3$. The gain in corrosion losses due to the presence of Fe(III) cations, especially in cold solutions, may be considerable [1–3]. Reduction of Fe(III) cations with metallic iron that occurs in diffusion mode is usually poorly hindered by corrosion inhibitors, which makes steel protection by this method inefficient [4].

The adverse effect of Fe(III) cations on the protective effect of corrosion inhibitors can be overcome by replacing sulfuric acid solutions with $\text{H}_2\text{SO}_4 + \text{H}_3\text{PO}_4$ mixtures containing a formulation of IFKhAN-92 (a 1,2,4-triazole derivative), KNCS and urotropine in a 9:1:400 molar ratio of the components. Such inhibited solutions are resistant against the accumulation of Fe(III) cations at H_2SO_4 concentrations up to 60% of the total mass of acids in a solution [3].

The high efficiency of the inhibitor mixture containing IFKhAN-92 toward corrosion of steels in acid solutions is due to the specifics of its protection mechanism, which is largely determined by the ability of this compound to form a protective layer of a polymeric complex chemically bound to the metal surface [5]. This protective layer is capable of hindering the reduction of not only protons but also Fe(III) cations [4]. However, it remains unclear why this effect is observed in solutions of H_3PO_4 or its mixtures with H_2SO_4 with low concentrations of the latter, but not in H_2SO_4 solutions or in its mixtures with H_3PO_4 containing much H_2SO_4 . We believe that this phenomenon results from the ability of H_3PO_4 or its anions to form products with Fe(III) cations that have lower oxidizing ability than Fe(III) compounds formed in H_2SO_4 solutions.

It is believed that the $\text{H}_3\text{PO}_4\text{--H}_2\text{O}$ system at $C_{\text{H}_3\text{PO}_4} = 0.1\text{--}10$ mol/kg can contain a number of particles: H_3PO_4 , H^+ , H_2PO_4^- and $\text{H}_5\text{P}_2\text{O}_8^-$ [6, 7]. The composition of the $\text{H}_3\text{PO}_4\text{--H}_2\text{O}\text{--Fe(III)}$ system is more complex. According to literature data [8], phosphate complexes of iron in aqueous H_3PO_4 solutions are products of successive replacement of water molecules in iron hexahydrate $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ with H_2PO_4^- or HPO_4^{2-} ions. In the most acidic media with $C_{\text{H}^+} > 5$ M, the region where the $\text{Fe}(\text{H}_2\text{PO}_4)_2^{2+}$ complex predominates is observed at $C_{\text{H}_3\text{PO}_4} = 0.5\text{--}1$ M. Under these conditions, its content in solution is above 90%, which allows the spectral characteristics of a nearly pure compound to be obtained. The neutral phosphate complexes containing no water molecules have the composition $\text{Fe}(\text{H}_2\text{PO}_4)_3$. They are formed in the most concentrated H_3PO_4 solutions ($> 14\text{--}15$ mol/l). In the wide range of phosphoric acid concentrations between the ranges of existence of the partially substituted $\text{Fe}(\text{H}_2\text{PO}_4)_2^{2+}$ complex and the completely substituted anhydrous phosphate $\text{Fe}(\text{H}_2\text{PO}_4)_3$, aqua-phosphate complexes with intermediate compositions are formed most likely. In the region adjacent to anhydrous $\text{Fe}(\text{H}_2\text{PO}_4)_3$, the $\text{Fe}(\text{H}_2\text{PO}_4)_3\cdot\text{H}_2\text{O}$ hydrated phosphate exists. The $\text{H}_2\text{SO}_4\text{--H}_2\text{O}\text{--Fe(III)\text{--}Fe(II)}$ system was reported to contain complex Fe(III)-containing particles such as FeSO_4^+ , $\text{Fe}(\text{SO}_4)_2^-$, FeHSO_4^{2+} , and $\text{FeH}(\text{SO}_4)_2$ [9–12]. Based on the above, it is logical to assume that in phosphoric acid solutions, Fe(III) should be most fully bound into phosphate complexes that are most stable in solution and have the weakest oxidizing ability. Conversely, binding of Fe(III) into sulfate complexes can be not complete enough, and the resulting sulfate complexes should be stronger oxidants than phosphate ones.

This hypothesis can be confirmed by estimating the oxidizing ability of the Fe(III)/Fe(II) redox couple in $\text{H}_2\text{SO}_4\text{--H}_3\text{PO}_4$ mixtures with varied H_3PO_4 content.

Unfortunately, we failed to find any potentiometric studies of the $\text{H}_2\text{SO}_4\text{--H}_3\text{PO}_4\text{--H}_2\text{O--Fe(III)--Fe(II)}$ system in available literature, we could only find studies on the $\text{H}_2\text{SO}_4\text{--H}_2\text{O--Fe(III)--Fe(II)}$ system [9, 11]. It is noted that the formation of complexes of Fe cations with anions formed upon H_2SO_4 dissociation affects the electrode potentials observed in these media [9]. Furthermore, the potentiometry and cyclic voltammetry methods were used to study the $\text{H}_3\text{PO}_4\text{--H}_2\text{O--Fe(III)--Fe(II)}$ system [13]. It was shown for this system that an increase in H_3PO_4 content in solutions from 1 to 6 M decreases the $E_{\text{Fe(III)/Fe(II)}}$ redox potential by more than 0.05 V, which also confirms our hypothesis that Fe(III) phosphate complexes have lower oxidizing ability than its aqueous and sulfate complexes.

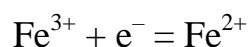
Experimental

Solutions were prepared from H_3PO_4 and H_2SO_4 of “chemically pure” grade and distilled water. H_3PO_4 solutions containing Fe(III) phosphates were obtained using the reaction of excess H_3PO_4 with Fe(OH)_3 precipitated with NaOH (“chemically pure” grade) from a FeCl_3 solution. The Fe(III) chloride solution was prepared from $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (“pure” grade). H_2SO_4 solutions containing iron sulfates were prepared from $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ (both of “chemically pure” grade). Due to technical difficulties in the preparation of H_3PO_4 solutions containing Fe(II) phosphates for potentiometric studies, they were replaced by solutions containing an equivalent concentration of FeSO_4 . In this approach, the maximum unaccounted content of SO_4^{2-} and PO_4^{3-} was 2.4% each of the total concentration of anions in solution, which allowed us to neglect this fact in the further discussion.

Potentiometric studies were performed in a temperature-controlled glass electrochemical cell YaSE-2. The accuracy of temperature control in the cell was $\pm 1^\circ\text{C}$. A smooth platinum (1.5 cm^2) working electrode and a saturated silver chloride reference electrode were used. The potential difference between the working and reference electrodes was determined using a PI-50 potentiostat. The working solutions were deaerated with argon (“chemically pure” grade) for 30 min both before and during the entire experiment. The potential of the platinum electrode in the working solution was measured in 30 min after the required temperature was established in the cell. In this measurement mode, the potential of the working electrode remained constant for at least the last 20 min. Electrode potentials are reported *versus* the standard hydrogen electrode.

Experimental results and discussion

The potential of a platinum electrode in a solution containing Fe(III) and Fe(II) is determined by the reaction:



It can be calculated from the active concentrations of the corresponding cations using the Nernst equation:

$$E_{\text{Fe(III)/Fe(II)}} = E_{\text{Fe(III)/Fe(II)}}^0 + \frac{RT}{F} \ln \frac{a_{\text{Fe(III)}}}{a_{\text{Fe(II)}}}$$

The standard electrode potential is $E_{\text{Fe(III)/Fe(II)}}^0 = 0.771$ V at 25°C, while $\frac{dE_{\text{Fe(III)/Fe(II)}}^0}{dT} = 0.00119$ V/K [14]. The use of the Nernst equation in this form, and particularly at high electrolyte concentrations, is difficult because the activity of any type of potential-determining ions in a solution is usually not related to their concentration by a simple relationship. The active concentrations of non-complexed iron cations in solution can be found using the activity coefficients calculated by the Debye–Hückel equation and the equilibrium constants that characterize complex compounds of Fe. Taking into account the complexity of the system concerned and the uncertainty of its chemical composition, this problem cannot be solved.

From the practical point of view, it is more appropriate to describe the processes that occur in acid solutions containing Fe cations using the real potential of the redox system established in a particular solution at equal starting concentrations of an oxidized and reduced forms of potential-determining ions, without consideration for the corrections for complexation, hydrolysis, and other processes [15]. For the system being studied, its real potential is most convenient for a qualitative interpretation of experimental data related to the complexation of potential-determining ions.

A potentiometric study of H₂SO₄ and H₃PO₄ solutions containing 0.05 M Fe(III), 0.05 M Fe(II), as well as their mixtures, has shown (Figure 1) that the potentials of a Pt electrode observed in these solutions at $t = 20$ – 95°C are considerably lower than the standard $E_{\text{Fe(III)/Fe(II)}}^0$ values for the same temperatures calculated from the data reported in [14]. The standard values at these temperatures are $E_{\text{Fe(III)/Fe(II)}} = 0.77$ – 0.85 V, in 2 M H₂SO₄ – 0.66 – 0.75 V, in 1 M H₂SO₄ and 1 M H₃PO₄ – 0.55 – 0.60 V, and in 2 M H₃PO₄ – 0.44 – 0.46 V, though, according to the Nernst equation, they should be similar at equal concentrations of the Fe(III) + Fe(II) mixture in these solutions. All this indicates that in the acids being studied, Fe(III) cations are bound by the anions of acid residues, resulting in a decrease in the oxidizing ability of these systems.

The highest oxidizing ability is observed in the H₂SO₄ solution containing an equimolar mixture of Fe(III) and Fe(II), whereas the H₃PO₄ solution shows the lowest oxidizing ability (Figure 1). As the H₃PO₄ content in the acid mixture increases, the oxidizing ability of the solutions decreases. The difference between the potentials of Pt in 2 M H₂SO₄ and 2 M H₃PO₄ is 0.22 V at 20°C and considerably higher, 0.29 V, at 95°C. The oxidizing ability of all the solutions studied increases with an increase in t . This effect is the strongest in H₂SO₄ alone and becomes weaker with an increase in the H₃PO₄ content in the acid mixture. In fact, an increase in t by 75°C in 2 M H₂SO₄ increases the potential of the Pt electrode almost by 0.09 V, in 1 M H₂SO₄ + 1 M H₃PO₄ by 0.05 V, and in 2 M H₃PO₄ by only 0.02 V. The likely reason of the observed effects is that phosphate

complexes of Fe(III) have higher stability than the sulfate complexes. As a result, the concentration of free Fe(III) cations in a sulfate solution is higher, which affects the oxidizing ability of these media. This is confirmed by the instability constants of complex compounds (pK_i) at $t = 20\text{--}30^\circ\text{C}$: judging by these values, Fe(III) cations generally form stronger complexes with phosphate anions ($pK_i([\text{FeHPO}_4]^+) = 9.75$; $pK_i([\text{FeH}_2\text{PO}_4]^{2+}) = 3.5$; $pK_i([\text{Fe}(\text{H}_2\text{PO}_4)_4]^-) = 9.15$ [16]) than with sulfate anions ($pK_i([\text{FeSO}_4]^+) = 4.02$ [12], 4.18 [16]; $pK_i([\text{FeHSO}_4]^{2+}) = 2.48$ [11]; $pK_i([\text{Fe}(\text{SO}_4)_2]^-) = 5.38$ [12], 7.4 [16]; $pK_i([\text{FeH}(\text{SO}_4)_2]) = 8.10$ [12]). Along with that, the oxidizing ability of Fe(III) phosphate complexes should be lower than that of sulfate complexes.

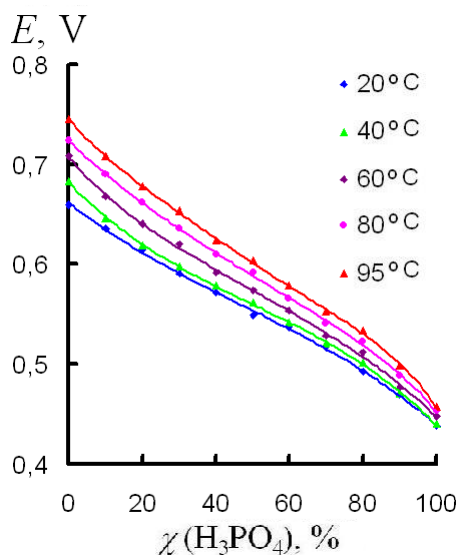


Figure 1. Potentials of a platinum electrode in argon-deaerated 2 M $\text{H}_2\text{SO}_4 + \text{H}_3\text{PO}_4$ solutions containing 0.05 M Fe(III) and 0.05 M Fe(II) depending on the H_3PO_4 molar fraction in acid mixtures at various temperatures.

A tenfold decrease in the content of the equimolar mixture of Fe(III) and Fe(II) in 1 M $\text{H}_2\text{SO}_4 + 1$ M H_3PO_4 nearly does not affect the potential of the Pt electrode in this solution (Figure 2), which well agrees with the Nernst relationship of potential *versus* the ratio of active concentrations of the oxidized and reduced forms of a redox couple. Its small growth is observed (*ca.* by 0.01 V), which apparently results from the different capabilities of Fe(III) and Fe(II) cations to undergo complexation with phosphate and sulfate anions. This simultaneously and to a different extent decreases the content of free Fe(III) and Fe(II) cations in the solution. Conversely, variation of the Fe(III)/Fe(II) ratio in the acid mixture considerably affects the oxidizing ability of the system (Figure 3). An increase in the Fe(III)/Fe(II) ratio by 4 orders increases E by 0.20–0.24 V. In this case, the higher the Fe(III) content in the solution, the more considerably the potential of the Pt electrode grows with an increase in temperature. In fact, at $C_{\text{Fe(III)}}/C_{\text{Fe(II)}} = 0.01$ an increase in

solution temperature by 75°C increases $E_{\text{Fe(III)/Fe(II)}}$ by 0.04 V, while at $C_{\text{Fe(III)}}/C_{\text{Fe(II)}} = 100$, by 0.08 V.

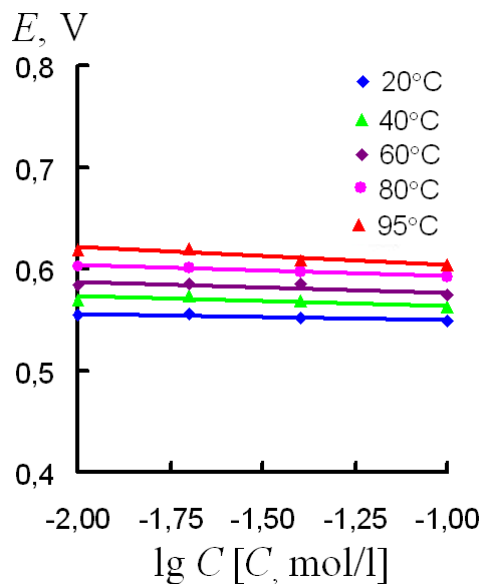


Figure 2. Potentials of a platinum electrode in argon-deaerated 1 M H_2SO_4 + 1 M H_3PO_4 solutions containing an equimolar Fe(III) + Fe(II) mixture depending on the total concentration of Fe cations.

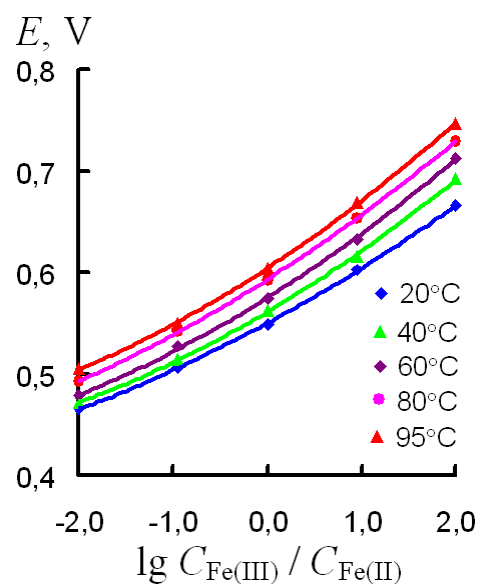


Figure 3. Potentials of a platinum electrode in argon-deaerated 1 M H_2SO_4 + 1 M H_3PO_4 solutions containing an 0.1 M Fe(III) + Fe(II) mixture depending on the Fe(III) / Fe(II) concentration ratio.

At a fixed content of the equimolar Fe(III) + Fe(II) mixture in solution, an increase in the content of the H₂SO₄ + H₃PO₄ mixture (1 : 1) somewhat decreases the potential of a Pt electrode (Figure 4). An increase in the content of the acid mixture from 1 M to 6 M decreases E by about 0.02 V. This is a result of more efficient binding of Fe(III) cations into complexes in their concentrated solutions.

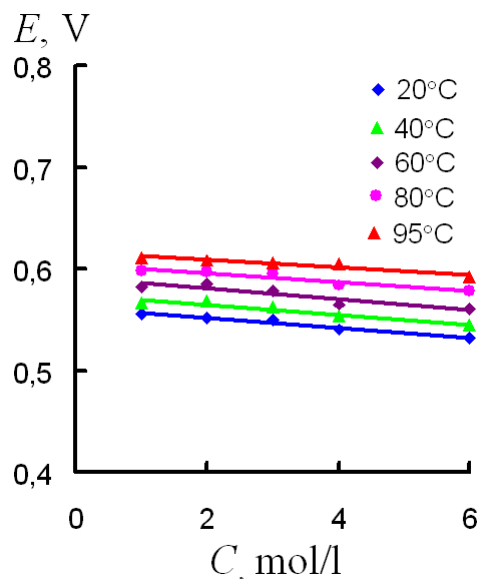


Figure 4. Potentials of a platinum electrode in argon-deaerated H₂SO₄ + H₃PO₄ (1 : 1) solutions containing an 0.02 M Fe(III) + 0.02 M Fe(II) mixture depending on the total concentration of acids.

Thus, addition of H₃PO₄ to H₂SO₄ solutions containing Fe(III) decreases their oxidizing ability due to Fe(III) binding into strong phosphate complexes possessing weak oxidizing properties. I.G. Gorichev *et al.* [17] attributed the effect of decreasing the redox potential of the H₂SO₄ + Fe(III) + Fe(II) system upon addition of H₃PO₄ and H₄P₂O₇ to differences in the degree of complexation of Fe(III) and Fe(II) cations in the presence of phosphate and pyrophosphate anions. A decrease in the redox potential of the H₂SO₄ + Fe(III) + Fe(II) system is also observed in the presence of complexing ligands, such as F⁻ and NCS⁻ [15]. The $E_{\text{Fe(III)/Fe(II)}}$ values in the HCl + Fe(III) + Fe(II) system decrease upon addition of H₃PO₄ [15] and H₃AsO₄ introduced into the system as As₂O₅ [18], while those in the HClO₄ + Fe(III) + Fe(II) system decrease upon H₃AsO₄ addition [18]. It has been shown [18] that in the case of H₃AsO₄, the decrease in $E_{\text{Fe(III)/Fe(II)}}$ in acid solutions results from Fe(III) binding into [FeHAsO₄]⁺ ($pK_i = 10.3$) and [FeH₂AsO₄]²⁺ complexes ($pK_i = 4.02$). The $E_{\text{Fe(III)/Fe(II)}}$ value in H₃PO₄ solutions containing Fe cations can be decreased by addition of HF [13]. It was assumed that [PO₃F]²⁻ anions were formed in these solutions, which then gave complex compounds with Fe(III).

The $E_{\text{Fe(III)/Fe(II)}}$ values in solutions of various acids can be used to predict the ability of their anions to undergo complexation with iron cations. According to the data presented in

Table 1, HF has the greatest complexation ability, in good agreement with the literature data discussed above [13]. Conversely, binding Fe cations into acid complexes in HClO₄ and HNO₃ solutions apparently does not occur and the $E_{\text{Fe(III)/Fe(II)}}$ values match the standard value.

Table 1. Stationary potentials $E_{\text{Fe(III)/Fe(II)}}$ of a platinum electrode in various 1 N acids [19].

Acid	$E_{\text{Fe(III)/Fe(II)}}, \text{V}$	Acid	$E_{\text{Fe(III)/Fe(II)}}, \text{V}$
HF	0.55	H ₂ SO ₄	0.68
H ₃ PO ₄	0.59	HNO ₃	0.77
HCl	0.67	HClO ₄	0.78

The experimental studies that we performed confirm our hypothesis that phosphate complexes of Fe(III) have lower oxidizing ability than its aqueous and sulfate complexes. This effect is one of the reasons of efficient protection of low-carbon steel by composite inhibitors based on triazoles in H₃PO₄ or in mixtures on its basis containing Fe(III) in comparison with H₂SO₄ alone. Analysis of literature data that we performed allows us to assume that HF can be used as a promising alternative to H₃PO₄ in inhibited solutions of mineral acid mixtures stable against Fe(III) accumulation, since $E_{\text{Fe(III)/Fe(II)}}$ decreases most efficiently in the presence of HF. However, such a replacement would be hardly expedient in many cases due to the high toxicity of HF.

Attention should be paid to the fact that we performed these studies in solutions of acids containing not only a corrosive solution component, *i.e.*, Fe(III) salts, but also its reduced form, *i.e.*, Fe(II) salts. To a considerable extent, such systems simulate industrial etching acid solutions that accumulate both Fe(II) and Fe(III) salts during the treatment of steel items. As follows from the experimental results, accumulation of Fe(II) salts in solution would considerably decrease the oxidizing ability of Fe(III) cations.

The experimental results that we obtained are important for understanding the mechanism of protective action of acid corrosion inhibitors. A new indirect mechanism of action of solution anions on the protective effect of inhibitors has been shown. Solution anions bind the most corrosive particles of the medium, Fe(III) cations in this case, into complex compounds, thus decreasing their oxidizing ability. This effect appears to be sufficient to allow the protective inhibitor layers formed on steel surface to interfere with the reduction of corrosive particles.

Conclusions

1. The oxidizing capability of the H₂SO₄–H₃PO₄–H₂O system containing Fe(III) and Fe(II) decreases as the relative content of H₃PO₄ increases. The observed effect results from the formation of Fe(III) complexes with phosphate anions that are weaker oxidants than the corresponding hydrate and sulfate complexes.

2. Variation in the total content of the equimolar Fe(III) + Fe(II) mixture ($C = 0.01\text{--}0.10\text{ M}$) in $1\text{ M H}_2\text{SO}_4 + 1\text{ M H}_3\text{PO}_4$ nearly does not affect its oxidative ability. Conversely, an increase in the relative content of Fe(III) in the system considerably increases its oxidative potential. At a fixed concentration of the Fe(III) + Fe(II) mixture in the system (0.04 M), addition of an equimolar mixture of H_2SO_4 and H_3PO_4 (up to 6 M) somewhat decreases the oxidative properties of the system.
3. Phosphate complexes of Fe(III) have lower oxidizing ability than its aqueous and sulfate complexes. This effect is one of the reasons of efficient protection of low-carbon steel by composite inhibitors based on triazoles in H_3PO_4 or in its mixtures with H_2SO_4 containing Fe(III) in comparison with similar solutions of H_2SO_4 alone.

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