

# Inhibitory protection of low-carbon steel in a mixed solution of hydrochloric and phosphoric acids containing Fe(II) and Fe(III) salts<sup>1</sup>

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## Abstract

The effect of Fe(III) and Fe(II) salts on the corrosion of low-carbon steel 08PS in 1 M HCl + 1 M H<sub>3</sub>PO<sub>4</sub>, 2 M HCl and 2 M H<sub>3</sub>PO<sub>4</sub> was studied in the temperature range of  $t=25-100^{\circ}\text{C}$ . Mixtures of chemical compounds containing IFKhAN-92, a 1,2,4-triazole derivative, were studied as steel corrosion inhibitors in these environments. The inhibitory effect of the binary formulation IFKhAN-92 + KNCS (molar ratio of components 9:1) and the three-component formulation IFKhAN-92 + KNCS + hexamethylenetetramine (HMT) (9:1:400) on steel corrosion in these media was considered. The IFKhAN-92 + KNCS + HMT formulation was shown to be promising for the protection of low-carbon steel in 1 M HCl + 1 M H<sub>3</sub>PO<sub>4</sub>. It was found that under the experimental conditions, the three-component mixture provides protection for steel in 1 M HCl + 1 M H<sub>3</sub>PO<sub>4</sub>, even if the solution contains Fe(III), Fe(II) salts or their mixtures. The protective effects of the inhibitors studied are weaker under similar conditions in 2 M HCl alone. The stronger inhibition of steel corrosion by the composite inhibitors based on IFKhAN-92 in HCl + H<sub>3</sub>PO<sub>4</sub> solutions containing Fe(III) salts in comparison with similar solutions of HCl alone is largely due to the binding of Fe(III) cations by phosphate anions into complexes, which significantly reduces their chemical activity, and hence the corrosion rate of steel.

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**Keywords:** acid corrosion, hydrochloric acid, phosphoric acid, corrosion inhibitors, triazoles, low carbon steel, iron(III) chloride, iron(III) phosphate, iron(II) chloride, iron(II) phosphate.

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## Introduction

Hydrochloric acid solutions are used in various fields of industry, including oil and gas production, metallurgy, and public utilities [1–12]. They are used to enhance the production of hydrocarbon raw materials from oil- and gas-bearing formations and to remove thermal scale, corrosion products, and mineral deposits from the internal surfaces of steel equipment. During these technological operations, corrosive HCl solutions come into contact with metal parts of the equipment. Steel equipment cannot be operated under such conditions without special protective measures. A technologically simple and inexpensive way to protect steels in HCl solutions is to use corrosion inhibitors, such as organic compounds or their mixtures with inorganic compounds [13–18].

The inhibitors of acid corrosion used under operating conditions should maintain the ability to protect steel products and structures in contact with acid solutions even if Fe(II) salts and especially Fe(III) salts accumulate in the corrosive environment [19–22]. Otherwise, during long-term use of acid solutions in contact with steel structures or products formed due to their corrosion, Fe(II) and Fe(III) salts will accumulate in them, which can significantly weaken the protection by the inhibitor.

In our opinion, a solution to this problem is to find alternative inhibited acid media that are resistant to the accumulation of Fe(III) cations in them. Acid media containing phosphate anions are, to a large extent, unique in this regard [23]. The use of composite inhibitors containing a 3-substituted 1,2,4-triazole, IFKhAN-92, can effectively suppress the corrosion of steels even in the case of significant accumulation of Fe(III) salts in them. In many aspects, the issue of the stability of such composite inhibitors to the presence of Fe(II) salts in a solution, which necessarily accumulate in it during its use, remains open.

In view of the above, it is of importance to identify the effect of Fe(II) cations and combinations of Fe(II) and Fe(III) cations on the corrosion of low-carbon steel in a mixture of hydrochloric and phosphoric acids in the presence of mixed inhibitors based on IFKhAN-92. The following mixtures were studied, which significantly slow down the corrosion of low-carbon steel in solutions of  $\text{H}_2\text{SO}_4 + \text{H}_3\text{PO}_4$  mixtures even with accumulated Fe(II) and Fe(III) salts [23]: the binary mixture IFKhAN-92 + KNCS (molar ratio of components 9:1) and the three-component mixture IFKhAN-92 + KNCS + hexamethylenetetramine (HMT) (9:1:400). To better understand the action of Fe cations on the protective effect of the inhibitors studied, similar studies were carried out in parallel in solutions of HCl and  $\text{H}_3\text{PO}_4$  alone.

## Experimental

The corrosion rate of 08PS low-carbon steel (composition, wt.%: C – 0.08; Mn – 0.5; Si – 0.11; P – 0.035; S – 0.04; Cr – 0.1; Ni – 0.25; Cu – 0.25; As – 0.08) in 1 M HCl + 1 M  $\text{H}_3\text{PO}_4$ , 2 M HCl and 2 M  $\text{H}_3\text{PO}_4$  solutions was determined based on the weight loss of strip samples measuring 50 mm × 20 mm (no less than 3 samples per point) using 50 mL of an acid solution

per sample. The duration of each experiment was 2 hours. Before an experiment, the samples were cleaned using an abrasive wheel (ISO 9001, grit 60) and degreased with acetone.

The solutions were prepared using reagent grade acids (HCl and H<sub>3</sub>PO<sub>4</sub>) and distilled water. Acid solutions containing Fe(III) salts were prepared by reacting Fe(OH)<sub>3</sub>, precipitated with NaOH (reagent grade) from a FeCl<sub>3</sub> solution, with an excess of the corresponding acid. The solution of Fe(III) chloride was prepared from FeCl<sub>3</sub>·6H<sub>2</sub>O (“pure” grade). Solutions of HCl and H<sub>3</sub>PO<sub>4</sub> containing FeCl<sub>2</sub> and Fe<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>, respectively, were prepared by dissolving reduced iron (“pure” grade) in excess HCl and H<sub>3</sub>PO<sub>4</sub>. Freshly prepared solutions were used.

Due to the low solubility of IFKhAN-92, it was added to the acid solutions as a solution in ethanol. The ethanol concentration in the resulting acid solution was 0.24 mol/L.

The efficiency of inhibitors was assessed in terms of the corrosion inhibition coefficient  $\gamma = k_0/k_{in}$ , where  $k_0$  and  $k_{in}$  are the corrosion rates in the background solution and in a solution with an additive under study, respectively. To calculate the  $\gamma$  values, a solution containing only Fe(III) and/or Fe(II) cations in the appropriate concentration as the additives was used as the background solution.

## Results and Discussion

In 1 M HCl + 1 M H<sub>3</sub>PO<sub>4</sub>, the corrosion rate of 08PS steel ( $k$ ) increases with an increase in temperature ( $t$ ). Increasing  $t$  from 25 to 100°C accelerates corrosion by a factor of 820 (Table 1). The presence of 0.05 M Fe(III) in this corrosive environment at  $t \leq 60^\circ\text{C}$  stimulates steel corrosion, but at higher temperatures it slows it down slightly. The acceleration of corrosion due to the presence of Fe(III) salts is most pronounced at 40°C, where it increases 2.4-fold. Addition of 0.05–0.25 M Fe(II) to such solutions has virtually no effect on the  $k$  value of steel. The presence of Fe(II) alone in a corrosive environment does not affect steel corrosion significantly, either. It is only at 25°C that a decrease in the  $k$  of steel due to the presence of 0.30–0.50 M Fe(II) in the environment is noted. At  $t \leq 60^\circ\text{C}$ , steel corrosion in a solution containing 0.25 M Fe(II) + 0.05 M Fe(III) develops faster than in a medium containing 0.30 M Fe(II), which is a result of the stimulating effect Fe(III) cations. This effect is not observed at higher  $t$  values.

In 2 M HCl, the corrosion rate of 08PS steel also increases with increasing  $t$ . Increasing the temperature by 75°C accelerates corrosion by a factor of 920 (Table 2). In this environment, the presence of 0.05 M Fe(III) at  $t \leq 60^\circ\text{C}$  stimulates steel corrosion. Addition of 0.05–0.25 M Fe(II) to the acid solution ( $t \leq 60^\circ\text{C}$ ) reduces the  $k$  value of steel. Under the same conditions, the presence of 0.30–0.50 M FeCl<sub>2</sub> in alone in the corrosive environment slightly reduces the  $k$  value of steel in comparison with the acid solution itself containing no Fe salts. In hotter HCl solutions ( $t \geq 80^\circ\text{C}$ ), the effect of the presence of Fe(III) and/or Fe(II) chlorides on steel corrosion is insignificant.

**Table 1.** Corrosion rates of 08PS steel ( $k$ , g/(m<sup>2</sup>·h)) in 1 M HCl + 1 M H<sub>3</sub>PO<sub>4</sub> in the presence of Fe(II) and Fe(III) salts.

$C_{\text{Fe(II)}}, \text{M}$	$C_{\text{Fe(III)}}, \text{M}$	Temperature, °C				
		25	40	60	80	100
Without inhibitor						
0	0	1.2	2.5	24	370	980
0	0.05	1.6	6.0	31	350	970
0.05	0.05	1.8	6.0	36	350	970
0.10	0.05	1.8	6.0	36	350	970
0.15	0.05	1.8	6.0	36	350	970
0.20	0.05	1.8	6.0	36	360	970
0.25	0.05	1.8	6.0	36	380	970
0.30	0	0.85	2.5	28	380	970
0.50	0	0.84	2.5	26	370	930
4.5 mM IFKhAN-92+0.5 mM KNCS						
0	0	0.31	0.33	0.61	0.84	5.4
0	0.05	0.80	2.1	5.4	7.7	9.0
0.05	0.05	0.88	2.1	5.2	12	35
0.10	0.05	0.73	1.9	4.8	12	35
0.15	0.05	0.57	1.9	4.8	12	30
0.20	0.05	0.45	1.6	4.7	12	30
0.25	0.05	0.47	1.6	4.7	11	21
0.30	0	0.23	0.78	0.37	1.2	8.3
0.50	0	0.28	0.95	0.26	1.3	11
4.5 mM IFKhAN-92+0.5 mM KNCS+200 mM HMT						
0	0	0.27	0.31	0.53	0.85	2.7

0	0.05	0.29	0.68	0.98	2.4	13
0.05	0.05	0.29	0.53	0.71	2.5	14
0.10	0.05	0.29	0.55	0.78	1.6	14
0.15	0.05	0.30	0.48	0.73	1.9	12
0.20	0.05	0.33	0.45	0.68	2.4	12
0.25	0.05	0.34	0.42	0.62	2.5	8.4
0.30	0	0.19	0.14	0.34	1.2	2.7
0.5	0	0.19	0.21	0.28	0.85	2.7

**Table 2.** Corrosion rates of 08PS steel ( $k$ , g/(m<sup>2</sup>·h)) in 2 M HCl in the presence of Fe(II) and Fe(III) salts.

$C_{\text{Fe(II)}}, \text{M}$	$C_{\text{Fe(III)}}, \text{M}$	Temperature, °C				
		25	40	60	80	100
Without inhibitor						
0	0	1.3	9.6	60	570	1200
0	0.05	5.2	13	75	580	1100
0.05	0.05	5.7	11	64	580	1100
0.10	0.05	5.9	11	64	570	1200
0.15	0.05	5.0	11	62	570	1200
0.20	0.05	4.7	7.6	62	570	1200
0.25	0.05	4.7	7.3	59	570	1200
0.30	0	0.69	4.9	56	580	1200
0.50	0	0.83	5.3	50	550	1100
4.5 mM IFKhAN-92+0.5 mM KNCS						
0	0	0.35	0.43	0.70	3.1	14
0	0.05	5.2	8.1	9.9	14	45
0.05	0.05	5.0	8.0	10	14	45
0.10	0.05	4.0	7.7	9.9	14	52
0.15	0.05	3.4	7.7	9.4	14	53
0.20	0.05	2.7	7.7	9.2	14	52
0.25	0.05	1.8	7.6	8.3	14	48

0.30	0	0.28	0.48	1.1	1.6	1.9
0.50	0	0.23	0.59	1.3	1.4	1.8
4.5 mM IFKhAN-92+0.5 mM KNCS+200 mM HMT						
0	0	0.25	0.47	0.73	3.6	16
0	0.05	5.0	8.2	9.9	15	45
0.05	0.05	4.9	7.8	11	15	46
0.10	0.05	4.9	7.8	11	15	53
0.15	0.05	4.7	7.8	9.9	14	54
0.20	0.05	4.7	7.8	9.9	14	53
0.25	0.05	4.5	7.6	9.5	14	51
0.30	0	0.35	0.4	0.62	1.4	1.8
0.50	0	0.32	0.54	0.95	1.2	1.6

In 2 M H<sub>3</sub>PO<sub>4</sub>, unlike in the media discussed above, an increase in  $t$  by 75°C accelerates steel corrosion by a factor of 110 only (Table 3). The presence of 0.05 M Fe(III) in this acid at  $t \leq 40^\circ\text{C}$  stimulates steel corrosion, but at higher temperatures it hinders corrosion. The effect of adding 0.05–0.25 M Fe(II) to these environments on the  $k$  value of steel is not straightforward; depending on the conditions, corrosion accelerates or slows down, but this effect is not essential. In 2 M H<sub>3</sub>PO<sub>4</sub> (25–80°C) at  $C_{\text{Fe(II)}}=0.30\text{--}0.50$  M, the value of  $k$  is slightly smaller than in the solution without Fe phosphates.

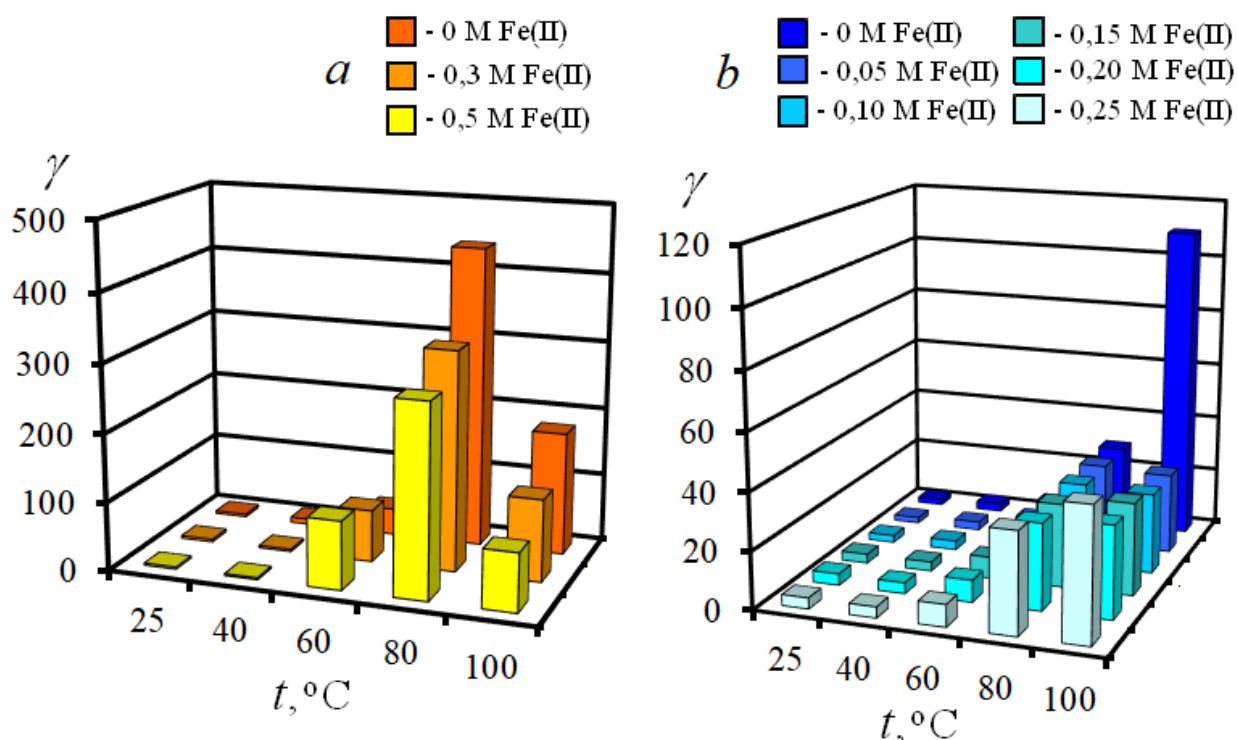
**Table 3.** Corrosion rates of 08PS steel ( $k$ , g/(m<sup>2</sup>·h)) in 2 M H<sub>3</sub>PO<sub>4</sub> in the presence of Fe(II) and Fe(III) salts.

$C_{\text{Fe(II)}}, \text{M}$	$C_{\text{Fe(III)}}, \text{M}$	Temperature, °C				
		25	40	60	80	100
Without inhibitor						
0	0	3.2	16	91	280	341
0	0.05	6.9	20	66	180	260
0.05	0.05	5.1	18	64	170	240
0.1	0.05	5.2	18	63	160	230
0.15	0.05	5.4	18	59	150	240
0.2	0.05	5.5	18	59	180	240
0.25	0.05	5.8	18	59	200	300

0.3	0	3.8	13	43	220	370
5	0	2.8	12	59	220	350
4.5 mM IFKhAN-92+0.5 mM KNCS						
0	0	0.44	0.49	0.24	0.35	1.0
0	0.05	0.81	0.49	0.35	0.78	42
0.05	0.05	0.81	0.23	0.18	0.65	61
0.10	0.05	0.81	0.45	0.16	0.89	70
0.15	0.05	0.93	0.45	0.20	1.3	67
0.20	0.05	0.95	0.44	0.18	1.3	64
0.25	0.05	0.74	0.43	0.18	2.6	32
0.30	0	0.33	0.3	0.12	0.36	5.8
0.50	0	0.31	0.51	0.28	0.52	5.9
4.5 mM IFKhAN-92+0.5 mM KNCS+200 mM HMT						
0	0	0.26	0.39	0.29	0.33	0.75
0	0.05	0.41	0.42	0.56	0.60	40
0.05	0.05	0.39	0.40	0.56	0.62	58
0.10	0.05	0.39	0.40	0.56	0.84	62
0.15	0.05	0.39	0.40	0.57	1.2	62
0.20	0.05	0.39	0.40	0.65	1.8	61
0.25	0.05	0.37	0.40	0.62	2.6	28
0.30	0	0.20	0.25	0.42	0.51	4.0
0.50	0	0.19	0.38	0.46	0.58	4.5

In 1 M HCl+1 M H<sub>3</sub>PO<sub>4</sub>, addition of the composite inhibitor comprising 4.5 mM IFKhAN-92+0.5 mM KNCS effectively protects 08PS steel, slowing down corrosion by a factor of 3.9–440 (Table 1, Figure 1). In this environment, the presence of 0.05 M Fe(III) significantly accelerates the corrosion of steel. In the absence of Fe(III) salts in 1 M HCl+1 M H<sub>3</sub>PO<sub>4</sub> (25–100°C), the *k* value of steel is 0.31–5.4 g/(m<sup>2</sup>·h), while it is

higher if they are present: 0.80–9.0 g/(m<sup>2</sup>·h). Addition of 0.05–0.25 M Fe(II) to the solution at  $t \leq 60^\circ\text{C}$  slightly reduces the  $k$  value of the metal, but at higher temperatures it increases this value. It is important that in 1 M HCl+1 M H<sub>3</sub>PO<sub>4</sub>+4.5 mM IFKhAN-92+0.5 mM KNCS, both in the absence of Fe salts and in the presence of Fe(III) or Fe(III)+Fe(II), in the selected  $t$  range (up to 100°C) the maximum efficiency of the two-component inhibitor is not achieved or is observed at temperatures close to 80°C. Due to this, it can be formally characterized as a high-temperature inhibitor [20]. In the same environment containing only Fe(II) salts, at  $t=25\text{--}80^\circ\text{C}$ , the  $k$  values are low. Even at the highest concentration of  $C_{\text{Fe(II)}}=0.50$  M, the maximum value is  $k=1.3$  g/(m<sup>2</sup>·h).

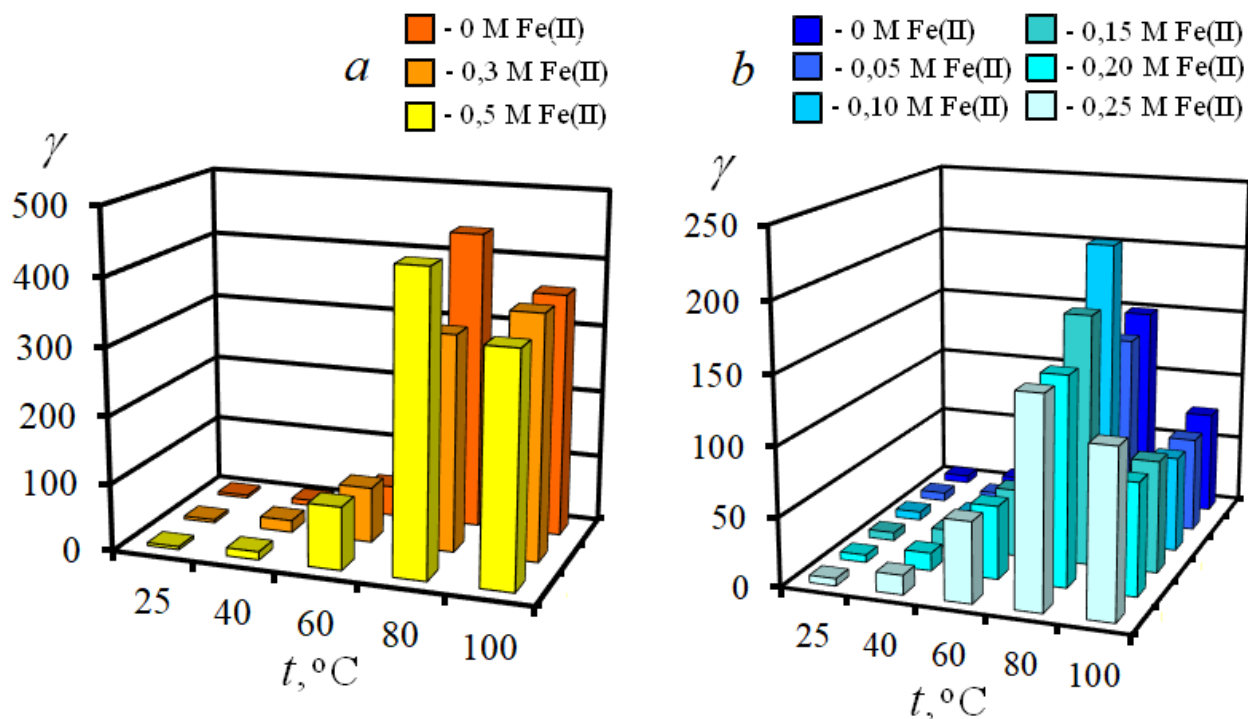


**Figure 1.** Corrosion inhibition coefficients of 08PS steel in 1 M HCl+1 M H<sub>3</sub>PO<sub>4</sub> (a) and 1 M HCl+1 M H<sub>3</sub>PO<sub>4</sub>+0.05 M Fe(III) (b) with addition of 4.5 mM IFKhAN-92+0.5 mM KNCS in the presence of various concentrations of Fe(II) salts.

The corrosion of steel in 1 M HCl+1 M H<sub>3</sub>PO<sub>4</sub> is better inhibited by the three-component mixture, 4.5 mM IFKhAN-92+0.5 mM KNCS+200 mM HMT (Table 1, Figure 2), which reduces the  $k$  value by a factor of 4.4–440. The presence of 0.05 M Fe(III) in this environment decreases the protective effect of the three-component inhibitor, the  $k$  value of steel being 0.29–13 g/(m<sup>2</sup>·h) versus 0.27–2.7 g/(m<sup>2</sup>·h) without this salt. Addition of 0.05–0.25 M Fe(II) to the solution at  $t \leq 60^\circ\text{C}$  reduces the  $k$  value of steel, but at higher temperatures the effect of this additive on steel corrosion is less significant. In all the systems discussed above, at  $t=25\text{--}100^\circ\text{C}$ , the maximum efficiency of the three-component formulation is not lower than that at 80°C, so it can be characterized as a high-temperature



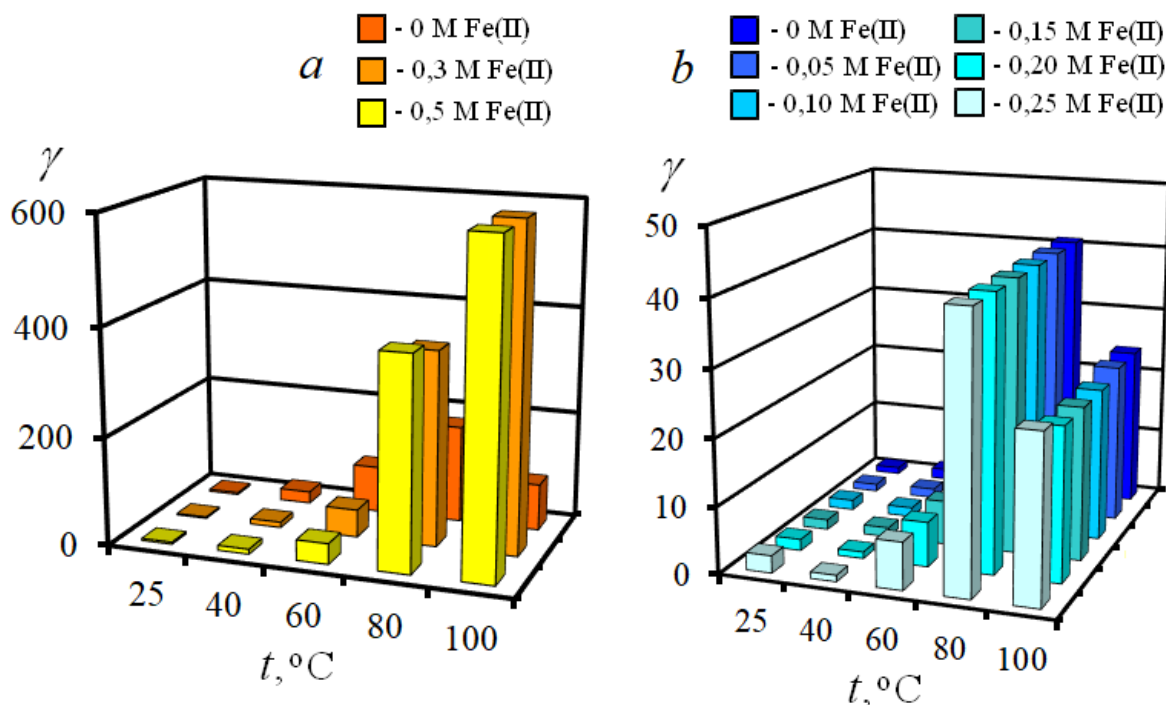
inhibitor. In 1 M HCl+1 M H<sub>3</sub>PO<sub>4</sub> containing Fe(II) salts alone, in the range  $t=25–100^{\circ}\text{C}$  the value of  $k$  is  $\leq 2.7 \text{ g}/(\text{m}^2\cdot\text{h})$ , which suggests that they have no adverse effect on corrosion.



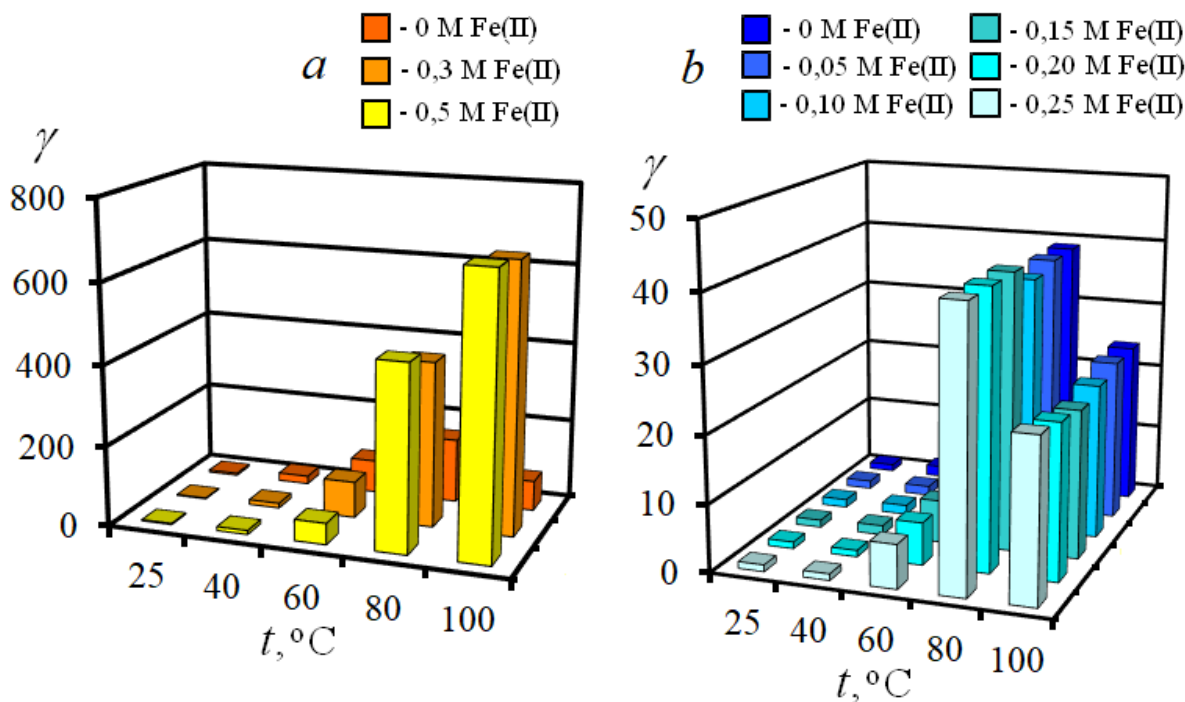
**Figure 2.** Corrosion inhibition coefficients of 08PS steel in 1 M HCl+1 M H<sub>3</sub>PO<sub>4</sub> (a) and 1 M HCl+1 M H<sub>3</sub>PO<sub>4</sub>+0.05 M Fe(III) (b) with addition of 4.5 mM IFKhAN-92+0.5 mM KNCS+200 mM HMT in the presence of various concentrations of Fe(II) salts.

In solutions containing Fe(III) or Fe(III)+Fe(II), at  $t \geq 80^{\circ}\text{C}$ , the protective effects of this mixture are stronger than those of the binary mixture IFKhAN-92+KNCS. Under the most drastic conditions ( $t=100^{\circ}\text{C}$ ),  $k \leq 14 \text{ g}/(\text{m}^2\cdot\text{h})$ , a satisfactory value, given the high temperature of the corrosive environment. From a practical point of view, it is more important that  $k \leq 2.5 \text{ g}/(\text{m}^2\cdot\text{h})$  at  $t \leq 80^{\circ}\text{C}$  in this environment.

In 2 M HCl, addition of mixed inhibitors, *i.e.*, 4.5 mM IFKhAN-92+0.5 mM KNCS or 4.5 mM IFKhAN-92+0.5 mM KNCS+200 mM HMT, slows down steel corrosion in the entire studied  $t$  range by a factor of 3.7–180 or 5.2–160, respectively (Table 2, Figure 3 and 4). Addition of 0.30–0.50 M Fe(II) does not worsen the protective effects of these inhibitors significantly. In contrast, addition of 0.05 M Fe(III) or 0.05 M Fe(III)+0.05–0.25 M Fe(II) to this medium greatly reduces the efficiency of both inhibitors studied.

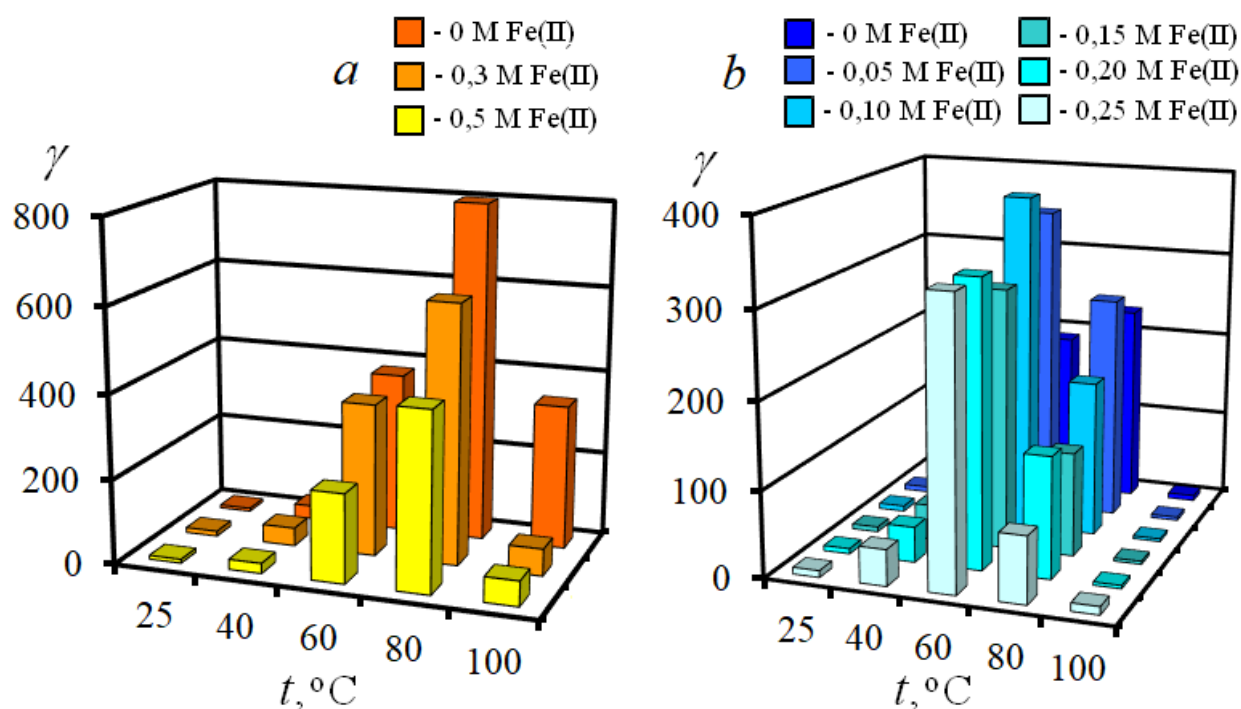


**Figure 3.** Corrosion inhibition coefficients of 08PS steel in 2 M HCl (a) and 2 M HCl+0.05 M Fe(III) (b) with addition of 4.5 mM IFKhaN-92+0.5 mM KNCS in the presence of various concentrations of Fe(II) salts.

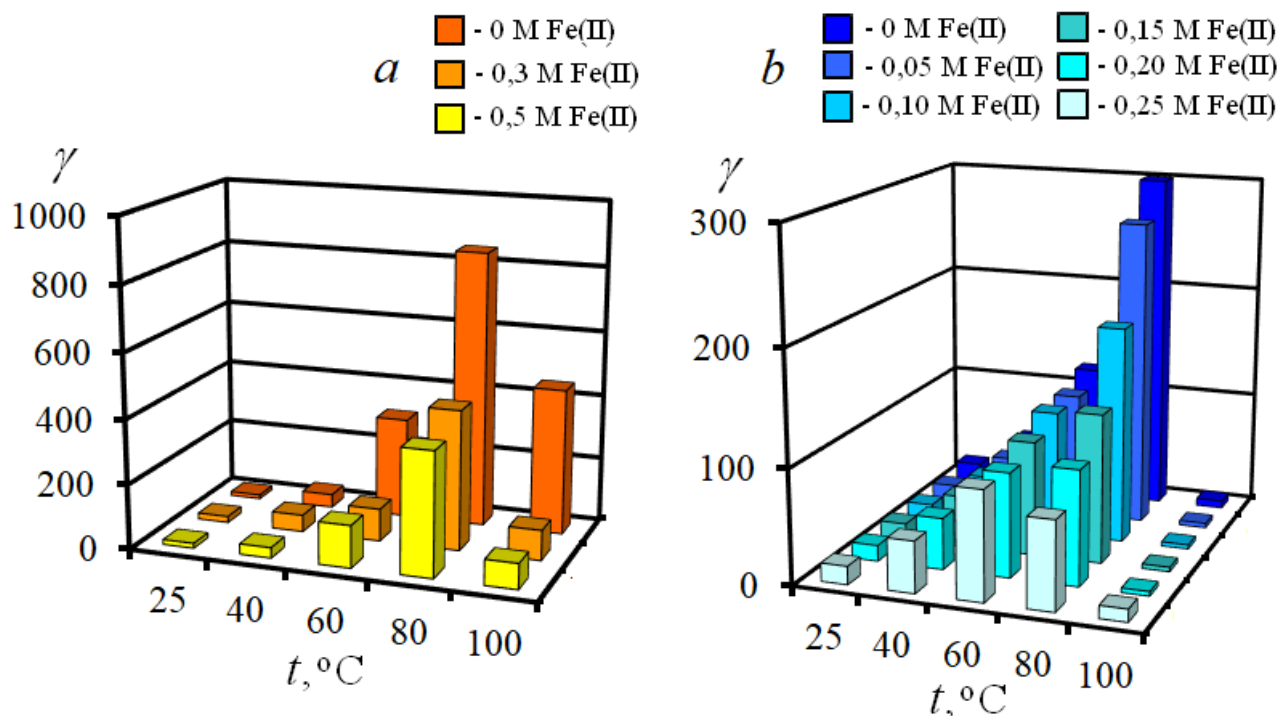


**Figure 4.** Corrosion inhibition coefficients of 08PS steel in 2 M HCl (a) and 2 M HCl+0.05 M Fe(III) (b) with addition of 4.5 mM IFKhaN-92+0.5 mM KNCS+200 mM HMT in the presence of various concentrations of Fe(II) salts.

In 2 M H<sub>3</sub>PO<sub>4</sub>, the addition of 4.5 mM IFKhAN-92+0.5 mM KNCS inhibits the corrosion of 08PS steel by a factor of 7.3–800, while the addition of 4.5 mM IFKhAN-92+0.5 mM KNCS+200 mM HMT, by a factor of 12–850 (Table 3, Figure 5 and 6). Addition of 0.05 M Fe(III) or 0.05 M Fe(III)+0.05–0.25 M Fe(II) to this medium slightly reduces the efficiency of both inhibitors at  $t=25\text{--}80^\circ\text{C}$ . In such systems, the corrosion rates are  $k=0.74\text{--}2.6$  and  $0.37\text{--}2.6$  g/(m<sup>2</sup>·h) for two- and three-component inhibitors, which can be considered a good result. However, at  $t=100^\circ\text{C}$ , both inhibitors significantly lose their steel protection efficiency. If Fe(II) itself is added to 2 M H<sub>3</sub>PO<sub>4</sub>, two- and three-component inhibitors maintain satisfactory protection at temperatures up to 100°C, while the  $k$  values are  $\leq 5.9$  and 4.5 g/(m<sup>2</sup>·h), respectively.



**Figure 5.** Corrosion inhibition coefficients of 08PS steel in 2 M H<sub>3</sub>PO<sub>4</sub> (a) and 2 M H<sub>3</sub>PO<sub>4</sub>+0.05 M Fe(III) (b) with addition of 4.5 mM IFKhAN-92+0.5 mM KNCS in the presence of various concentrations of Fe(II) salts.



**Figure 6.** Corrosion inhibition coefficients of 08PS steel in 2 M  $\text{H}_3\text{PO}_4$  (a) and 2 M  $\text{H}_3\text{PO}_4 + 0.05$  M  $\text{Fe(III)}$  (b) with addition of 4.5 mM IFKhAN-92+0.5 mM KNCS+200 mM HMT in the presence of various concentrations of  $\text{Fe(II)}$  salts.

Thus, the three-component mixture IFKhAN-92 + KNCS + HMT (9:1:400) developed by us is efficient in the protection of low-carbon steel 08PS in 1 M  $\text{HCl} + 1$  M  $\text{H}_3\text{PO}_4$  in the range  $t = 25\text{--}100^{\circ}\text{C}$ . This mixed inhibitor is fairly stable with respect to the accumulation of high concentrations of  $\text{Fe(III)}$  and  $\text{Fe(II)}$  salts and their mixtures in 1 M  $\text{HCl} + 1$  M  $\text{H}_3\text{PO}_4$ . Although some acceleration of corrosion is often observed in the presence of these salts in 1 M  $\text{HCl} + 1$  M  $\text{H}_3\text{PO}_4$ , the  $k$  values remain low, especially in comparison with the background media. For example, at temperatures up to 100  $^{\circ}\text{C}$  in the presence of 0.05 M  $\text{Fe(III)}$  the value of  $k$  is  $\leq 13$   $\text{g}/(\text{m}^2 \cdot \text{h})$ ; in the presence of 0.05 M  $\text{Fe(III)} + 0.05\text{--}0.25$  M  $\text{Fe(II)}$ ,  $k \leq 14$   $\text{g}/(\text{m}^2 \cdot \text{h})$ ; and in the presence of 0.30–0.50 M  $\text{Fe(II)}$ ,  $k \leq 2.7$   $\text{g}/(\text{m}^2 \cdot \text{h})$ . At temperatures up to 80  $^{\circ}\text{C}$  under any experimental conditions  $k$  is  $\leq 2.5$   $\text{g}/(\text{m}^2 \cdot \text{h})$ . The results obtained are of importance from the practical point of view, since we have developed an inhibited acid formulation for etching and cleaning low-carbon steels that is stable with respect to the accumulation of  $\text{Fe(III)}$  and  $\text{Fe(II)}$  salts. The inhibitor mixtures studied efficiently protect low-carbon steel in 2 M  $\text{H}_3\text{PO}_4$  containing  $\text{Fe(II)}$  at temperatures up to 100  $^{\circ}\text{C}$ , but in 2 M  $\text{H}_3\text{PO}_4$  containing  $\text{Fe(III)}$  or  $\text{Fe(III)} + \text{Fe(II)}$ , they are only efficient at temperatures up to 80  $^{\circ}\text{C}$ . In 2 M  $\text{HCl}$ , the presence of  $\text{Fe(III)}$  or  $\text{Fe(III)} + \text{Fe(II)}$  salts adversely affects the inhibition of steel corrosion in almost the entire  $t$  range studied. It is only in 1 M  $\text{HCl} + 1$  M  $\text{H}_3\text{PO}_4$ , even in the presence of  $\text{Fe}$  salts, that the three-component formulation slows down the corrosion of low-carbon steel satisfactorily in a wide range of  $t = 25\text{--}100^{\circ}\text{C}$ .

The nature of the stimulating effect of Fe(III) cations on the corrosion of steels in acid solutions is known. It is associated with their involvement as an additional oxidizing agent in the corrosion process [24], but the mechanisms for the effect of Fe(II) salts on steel corrosion have not been discussed in publications. In our opinion, Fe(II) salts affect the corrosion process in two ways. The presence of Fe(II) salts in acid solutions can lead to a decrease in their solubility in the surface layer adjacent to the metal where they accumulate as corrosion products. This mechanism should slow down the anodic reaction of the metal and general corrosion of steel. On the other hand, the presence of Fe(II) salts in acid media can increase their density. In such environments, hydrogen gas bubbles are removed from the surface more easily, which facilitates the cathodic reaction, thus accelerating overall corrosion. In an acid environment, depending on its anionic composition, the concentration of Fe(II) salts in the solution and temperature, one of these effects may prevail, which would eventually determine whether corrosion is hindered or accelerated.

In hot acid solutions containing Fe(III) salts, a slowdown of corrosion is observed, which can largely be due to rapid reduction on steel of Fe(III) salts to Fe(II) salts quickly accumulating in the etching solution. Ultimately, the accumulation of Fe(II) salts in solution probably slows down corrosion. It is important to note that the presence of Fe(II) salts in a solution along with Fe(III) salts should diminish the oxidizing ability of Fe(III) cations, thus decreasing their corrosiveness towards steel.

In inhibited acid solutions, the stimulating effect of Fe(III) salts on steel corrosion is primarily due to the facilitation of steel cathodic reaction, similarly to the background media, caused by the reduction of Fe(III) cations [24]. The effect of Fe(II) salts on inhibited acid solutions can be twofold. On the one hand, Fe(II) cations in a solution can bind the inhibitor mixture components, thus complicating their adsorption on the steel surface and reducing their effectiveness. On the other hand, inclusion of Fe(II) cations in the composition of the polymolecular layer formed by molecules of the IFKhAN-92 inhibitor on a steel surface would improve the protective properties [25].

The reasons for the more efficient inhibitory protection of steel in acid environments containing phosphate anions in the presence of Fe(III) salts, in comparison with an individual HCl solution, are largely due to the ability of phosphate anions to form complex compounds with Fe(III) cations. In fact, Fe(III) phosphate complexes have smaller oxidizing ability and mobility compared to Fe(III) chloride and aqua complexes existing in HCl solutions, which decreases their corrosiveness towards steel [24, 26]. The role of HMT in the stronger protective effect of the three-component mixture in comparison with the binary composition of inhibitors is due to the fact that its molecules, along with phosphate anions, bind Fe(III) cations into complex compounds. Complex compounds of Fe(III) formed in solutions containing phosphate anions and HMT have low oxidizing ability, as we have shown in a potentiometric study of such media [26]. Ultimately, particles with low oxidizing ability are less corrosive towards steel, which makes it possible to provide efficient inhibitory protection when they are present in a corrosive environment.

## Conclusions

1. The mixed inhibitor IFKhAN-92 + KNCS + HMT (molar ratio of components 9:1:400) provides efficient protection of low-carbon steel in 1 M HCl + 1 M H<sub>3</sub>PO<sub>4</sub> containing Fe(III), Fe(II) salts, or their combinations.
2. Stronger inhibition of steel corrosion by mixed inhibitors based on IFKhAN-92 in solutions of HCl+H<sub>3</sub>PO<sub>4</sub> containing Fe(III) salts, in comparison with similar solutions of HCl alone, is largely due to the binding of Fe(III) cations by phosphate anions into complexes, which significantly reduces their chemical activity and, as a consequence, the effect on the corrosion process.
3. The results obtained are of importance for the practice, since based on a solution of a mixture of HCl and H<sub>3</sub>PO<sub>4</sub>, an inhibited acid formulation was suggested for etching and cleaning low-carbon steels, which is stable with respect to the accumulation of Fe(III) and Fe(II) salts. The optimal operating mode for such a solution encompasses temperatures up to 80°C inclusive. Moreover, even if such a formulation is overheated to 100°C, the mixed inhibitor IFKhAN-92 + KNCS + HMT (9:1:400) provides satisfactory protection of steel.

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