

Inhibitory protection of low-carbon steel in a mixed solution of sulfuric and phosphoric acids containing Fe(II) and Fe(III) salts[#]

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Abstract

The effect of Fe(III) and Fe(II) salts on the corrosion of 08PS low-carbon steel in 1 M H₂SO₄ + 1 M H₃PO₄, 2 M H₂SO₄, and 2 M H₃PO₄ solutions was examined in a wide temperature range, $t = 25\text{--}100^\circ\text{C}$. Formulations of compounds containing a 1,2,4-triazole derivative, IFKhAN-92, used as steel corrosion inhibitors in these environments were studied. The binary mixture of IFKhAN-92+KNCS (molar ratio of components 9:1) and a three-component mixture IFKhAN-92+KNCS+urotropine (9:1:400) were explored. Under the experimental conditions, two- and three-component corrosion inhibitors provide efficient protection of steel in 1 M H₂SO₄+1 M H₃PO₄ solution even if it contains a high concentration of Fe(III) and Fe(II) salts or mixtures thereof. The most significant protective effect is provided by the three-component inhibitor mixture. Under similar experimental conditions, the protective effects of the inhibitors in individual 2 M H₃PO₄ and especially in 2 M H₂SO₄ solutions are lower. The stronger inhibition of steel corrosion by the composite inhibitors based on IFKhAN-92 in H₂SO₄+H₃PO₄ solutions containing Fe(III) salts, in comparison with similar solutions of H₂SO₄ 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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Introduction

Solutions of mineral acids are widely used in modern industries [1–8], including oil and gas production, metallurgy, and public utilities. These media are used to enhance the production of hydrocarbons from oil and gas deposits and to remove scale, corrosion products, and

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mineral deposits from the internal surfaces of metal equipment. During these production operations, corrosive acid solutions come into contact with steel parts of the equipment used in the design of equipment. Steel equipment cannot be operated in such environments without special protective measures. The most common method of protecting steels in acids is the employment of corrosion inhibitors based on organic compounds or their mixtures [9–12].

An important production requirement for inhibitors of the acid corrosion of steels is that they should maintain efficient protection in the cases where Fe(II) salts and, especially, Fe(III) salts are accumulated in the corrosive environment [13–16]. Otherwise, during long-term contact of acid solutions with steel structures or products formed upon their corrosion, Fe(II) and Fe(III) salts are accumulated, pre-determining the weak inhibitory protection of the metal under such conditions.

We see a solution to this problem in finding alternative inhibited acid media resistant to the accumulation of Fe(III) cations in them. We have previously shown [17] that acid media containing phosphate anions are in many aspects unique in this regard. The corrosion of steel in these environments can be significantly suppressed by using composite inhibitors containing a 3-substituted 1,2,4-triazole, IFKhAN-92, even if a significant amount of Fe(III) salts is accumulated in the solution. However, the issue of the stability of such composite inhibitors in the presence of Fe(II) salts in the solution, which will necessarily accumulate in it during production operations, was left unattended. It is generally believed [13] that due to the accumulation of Fe(II) salts in acid pickling solutions the inhibitor is removed from the corrosive environment, which has an extremely adverse effect on the protection of metals.

In this context, it is of importance to identify the effect of Fe(II) cations and both Fe(II) and Fe(III) cations the present simultaneously on the corrosion of low-carbon steel in a mixture of sulfuric and phosphoric acids inhibited by IFKhAN-92-based formulations. The following inhibitors were studied: the IFKhAN-92+KNCS binary mixture (molar ratio of components 9:1) and the three-component mixture IFKhAN-92+KNCS+urotropine (9:1:400), which slow down the corrosion of steels in this environment significantly even if Fe(III) salts accumulate therein. To better understand the effect of Fe cations on the protective action of the inhibitors under study, similar studies were concurrently carried out in individual H₂SO₄ and H₃PO₄ solutions.

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 H₂SO₄+1 M H₃PO₄, 2 M H₂SO₄ and 2 M H₃PO₄ solutions was determined from 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 (H_2SO_4 and H_3PO_4) and distilled water. Acid solutions containing Fe(III) salts were prepared by reacting $\text{Fe}(\text{OH})_3$, precipitated with NaOH (reagent grade) from a FeCl_3 solution, with an excess of the corresponding acid. The solution of Fe(III) chloride was prepared from $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (“pure” grade). Solutions of H_2SO_4 and H_3PO_4 containing FeSO_4 and $\text{Fe}_3(\text{PO}_4)_2$, respectively, were prepared by dissolving reduced iron (“pure” grade) in excess H_2SO_4 and H_3PO_4 . Freshly prepared solutions were used.

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

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

Results and Discussion

The corrosion rate of 08PS steel (k) in the 1 M H_2SO_4 +1 M H_3PO_4 solution increases with temperature (t). An increase in temperature by 75°C speeds up corrosion by a factor of 180 (Table 1). The presence of 0.05 M Fe(III) in this corrosive environment at $t \leq 40^\circ\text{C}$ enhances steel corrosion but slows it down at higher temperatures. The maximum acceleration of corrosion, which is observed at 25°C, amounts to 30% of the value observed in the absence of Fe(III). Introducing additional 0.05–0.25 M Fe(II) into such a solution on the k of steel has a complex effect: depending on the conditions, the process can be accelerated or hindered. The effect of the presence of Fe(II) is most pronounced at $t = 80^\circ\text{C}$ and amounts to 38% of the k value observed in 1 M H_2SO_4 +1 M H_3PO_4 +Fe(III). The presence of Fe(II) alone in a corrosive environment is also ambiguous, but most often it accelerates corrosion. The maximum increase in corrosion losses due to the presence of Fe(II) alone is 27%. In general, it should be concluded that the presence of Fe(III) and Fe(II) salts in 1 M H_2SO_4 +1 M H_3PO_4 solutions (25–100°C), as well as of both salts simultaneously, does not have a significant effect on the corrosion rate of 08PS steel in this environment.

Table 1. Corrosion rates of 08PS steel in 1 M H_2SO_4 +1 M H_3PO_4 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	4.3	8.6	58	220	790

$C_{\text{Fe(II)}}, \text{M}$	$C_{\text{Fe(III)}}, \text{M}$	Temperature, °C				
		25	40	60	80	100
0	0.05	5.5	10	53	210	710
0.05	0.05	5.3	11	50	200	830
0.10	0.05	6.2	11	52	130	830
0.15	0.05	5.7	11	55	140	940
0.20	0.05	5.4	10	56	180	950
0.25	0.05	5.2	10	56	200	960
0.30	0	5.1	8.5	52	230	1000
0.50	0	5.3	9.1	52	230	1000
4.5 mM IFKhAN-92+0.5 mM KNCS						
0	0	0.28	0.63	0.33	0.78	1.8
0	0.05	0.36	1.7	1.6	1.9	2.4
0.05	0.05	0.37	1.2	1.6	1.6	2.7
0.10	0.05	0.39	0.98	1.4	2.1	2.9
0.15	0.05	0.31	1.4	1.3	2.8	3.8
0.20	0.05	0.28	2.0	1.2	3.4	4.7
0.25	0.05	0.6	1.3	0.88	3.6	4.5
0.30	0	0.12	0.33	0.28	0.68	3.8
0.50	0	0.26	0.34	0.20	0.67	8.3
4.5 mM IFKhAN-92+0.5 mM KNCS+200 mM urotropine						
0	0	0.18	0.12	0.16	0.61	1.0
0	0.05	0.28	0.46	0.45	1.2	2.3
0.05	0.05	0.31	0.41	0.57	1.1	2.1
0.10	0.05	0.35	0.36	0.53	1.5	2.3

$C_{\text{Fe(II)}}, \text{M}$	$C_{\text{Fe(III)}}, \text{M}$	Temperature, °C				
		25	40	60	80	100
0.15	0.05	0.30	0.35	0.52	2.0	3.0
0.20	0.05	0.30	0.35	0.52	2.8	3.8
0.25	0.05	0.37	0.45	0.61	3.1	4.1
0.30	0	0.29	0.28	0.3	0.63	3.6
0.5	0	0.28	0.29	0.28	0.59	6.8

A similar behavior of the corrosion of 08PS steel is observed in individual 2 M H_2SO_4 and 2 M H_3PO_4 solutions. In these environments, an increase in temperature by 75°C speeds up steel corrosion by a factor of 570 and 11, respectively (Tables 2 and 3). In both environments, the presence of 0.05 M Fe(III) at $t \leq 40^\circ\text{C}$ facilitates steel corrosion, but slows it down at higher temperatures. Addition of extra 0.05–0.25 M Fe(II) to these environments affects the k factor of steel ambiguously: depending on the corrosion conditions, the process can be accelerated or hindered, but in any case, this effect is not significant. The presence of 0.30–0.50 M FeSO_4 in individual 2 M H_2SO_4 solution (25–80°C) slightly increases the k value of steel in comparison with the background acid, while in 2 M H_3PO_4 solution containing the same $C_{\text{Fe(II)}}$, the k value at $t = 40\text{--}80^\circ\text{C}$ becomes slightly smaller.

Table 2. Corrosion rates of 08PS steel in 2 M H_2SO_4 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	2.3	21	70	300	1300
0	0.05	5.2	8.9	36	270	1000
0.05	0.05	4.1	5.8	34	230	1100
0.10	0.05	4.1	6.8	21	250	1100
0.15	0.05	3.5	7.6	29	250	1100
0.20	0.05	3.3	9.3	35	250	1200

$C_{\text{Fe(II)}}, \text{M}$	$C_{\text{Fe(III)}}, \text{M}$	Temperature, °C				
		25	40	60	80	100
0.25	0.05	2.3	10	38	270	1200
0.30	0	2.3	23	83	380	1200
0.50	0	2.5	23	83	400	1300
4.5 mM IFKhAN-92+0.5 mM KNCS						
0	0	0.18	0.22	0.46	1.3	45
0	0.05	0.90	1.8	3.2	11	26
0.05	0.05	0.78	1.9	4.1	11	31
0.10	0.05	0.78	1.9	4.0	11	33
0.15	0.05	0.78	2.0	4.0	11	33
0.20	0.05	0.78	2.0	4.0	10	33
0.25	0.05	0.85	2.2	4.1	11	35
0.30	0	0.07	0.31	0.31	1.1	50
0.50	0	0.07	0.29	0.29	1.8	59
4.5 mM IFKhAN-92+0.5 mM KNCS+200 mM urotropine						
0	0	0.12	0.23	0.30	1.3	3.5
0	0.05	0.57	2.5	5.1	13	25
0.05	0.05	0.53	2.8	5.2	11	29
0.10	0.05	0.62	2.9	5.2	11	29
0.15	0.05	0.68	3.0	5.2	11	29
0.20	0.05	0.66	2.9	5.2	11	29
0.25	0.05	0.65	2.9	5.2	10	30
0.30	0	0.06	0.27	0.71	0.81	40
0.50	0	0.1	0.28	0.71	1.1	44

Table 3. Corrosion rates of 08PS steel in 2 M H₃PO₄ 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

$C_{\text{Fe(II)}}, \text{ M}$	$C_{\text{Fe(III)}}, \text{ M}$	Temperature, °C				
		25	40	60	80	100
4.5 mM IFKhAN-92+0.5 mM KNCS+200 mM urotropine						
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 H_2SO_4 +1 M H_3PO_4 solution, addition of the composite inhibitor comprising 4.5 mM IFKhAN-92+0.5 mM KNCS protects 08PS steel efficiently, slowing down corrosion by a factor of 15–440 (Table 1, Figure 1). In this environment, the presence of 0.05 M Fe(III) slightly accelerates the corrosion of steel. In the absence of Fe(III) salt in 1 M H_2SO_4 +1 M H_3PO_4 (25–100°C), the k value of steel is 0.28–1.8 g/(m²·h), while in its presence, it is higher and amounts to 0.36–2.4 g/(m²·h). The presence of 0.05–0.25 M Fe(II) in the solution further enhances metal corrosion in many cases, resulting in k =0.28–4.5 g/(m²·h). The highest values of steel corrosion inhibition coefficients for the IFKhAN-92+KNCS composition are observed in a mixed solution of acids in the absence of Fe salts. It is important that in the 1 M H_2SO_4 +1 M H_3PO_4 +4.5 mM IFKhAN-92+0.5 mM KNCS solution, both in the absence of Fe salts and in the presence of Fe(III) or Fe(III)+Fe(II), the maximum efficiency of the two-component inhibitor is not attained in the selected t range (up to 100°C), owing to which it can be characterized as a high-temperature inhibitor. In the same environment containing only Fe(II) salts, at t =25–80°C, the values of k became smaller than in the absence of these salts. It is only at t =100°C that the k value is higher. Despite this, even at the highest content of $C_{\text{Fe(II)}}=0.50$ M, $k=8.3$ g/(m²·h) and $\gamma=120$.

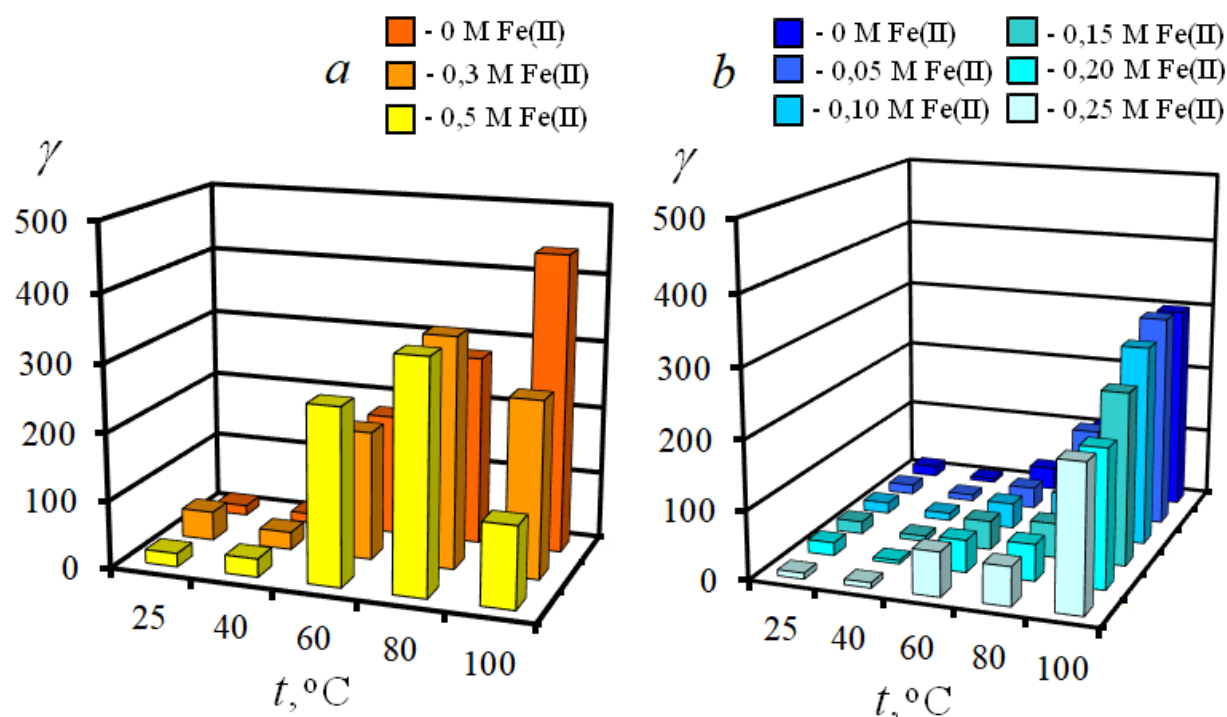


Figure 1. Corrosion inhibition coefficients of 08PS steel in 1 M H_2SO_4 +1 M H_3PO_4 (a) and 1 M H_2SO_4 +1 M H_3PO_4 +0.05 M Fe(III) (b) with addition of 4.5 mM IFKhAN-92+0.5 mM KNCS in the presence of various concentrations of Fe(II) salts.

The three-component composition 4.5 mM IFKhAN-92+0.5 mM KNCS+200 mM urotropine (Table 1, Figure 2), which reduces the k value by a factor of 24–790, slows down the corrosion of steel in 1 M H_2SO_4 +1 M H_3PO_4 more efficiently. The presence of 0.05 M Fe(III) or 0.05 M Fe(III) +0.05–0.25 M Fe(II) in this environment deteriorates the protective effect of the three-component inhibitor, yielding $k=0.28$ – 4.1 g/(m²·h) at $t=25$ – 100°C , a value which is slightly better than for the IFKhAN-92+KNCS mixture. In all the systems discussed above for a three-component composition at $t=25$ – 100°C , the maximum protective effect is not attained, due to which the inhibitor can be characterized as a high-temperature one. In the 1 M H_2SO_4 +1 M H_3PO_4 solution containing individual Fe(II) salts, in the range $t=25$ – 100°C the k values became slightly higher than in the absence of these salts. At $t\geq 80^\circ\text{C}$, the protective effect of this mixture is higher than that of the IFKhAN-92+KNCS binary mixture. Under the most severe conditions ($C_{\text{Fe(II)}}=0.50$ M, $t=100^\circ\text{C}$), $k=6.8$ g/(m²·h) and $\gamma=150$.

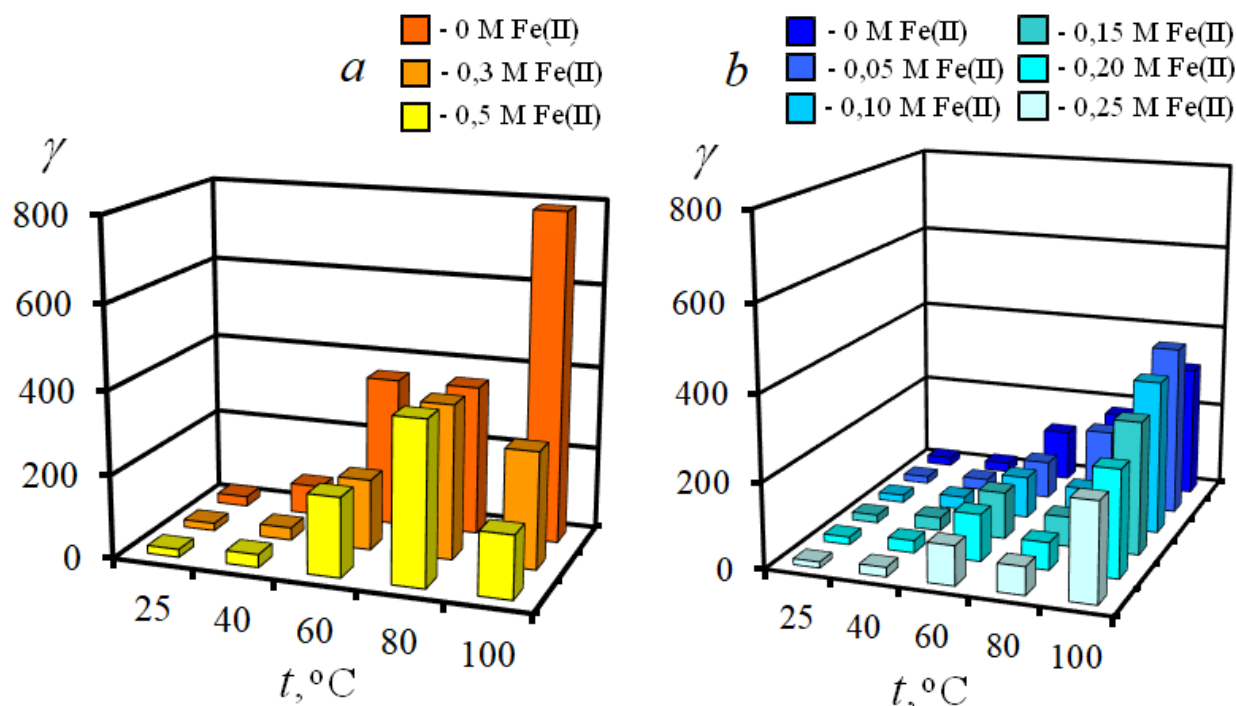


Figure 2. Corrosion inhibition coefficients of 08PS steel in 1 M H_2SO_4 +1 M H_3PO_4 (a) and 1 M H_2SO_4 +1 M H_3PO_4 +0.05 M Fe(III) (b) with addition of 4.5 mM IFKhAN-92+0.5 mM KNCS+200 mM urotropine in the presence of various concentrations of Fe(II) salts.

In 2 M H_2SO_4 solution, addition of the 4.5 mM IFKhAN-92+0.5 mM KNCS composite inhibitor is efficient in protecting 08PS steel at $t \leq 80^\circ\text{C}$, while addition of a three-component inhibitor – 4.5 mM IFKhAN-92+0.5 mM KNCS+200 mM urotropine – is efficient in the entire t range studied (Table 2, Figures 3 and 4). The addition of 0.05 M Fe(III) or 0.05 M Fe(III) +0.05–0.25 M Fe(II) to such a medium greatly deteriorates the efficiency of both inhibitors studied. In such systems ($t=25\text{--}100^\circ\text{C}$), $k=0.78\text{--}35$ and $0.53\text{--}30$ $\text{g}/(\text{m}^2\cdot\text{h})$ for two- and three-component inhibitors, respectively, which is significantly worse than in the 1 M H_2SO_4 +1 M H_3PO_4 system. In contrast, the presence of individual Fe(II) in 2 M H_2SO_4 does not change the protective effect of the studied inhibitors at $t \leq 80^\circ\text{C}$ significantly, but at $t=100^\circ\text{C}$ they lose efficiency to a considerable extent.

In 2 M H_3PO_4 solution, 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 addition of 4.5 mM IFKhAN-92+0.5 mM KNCS+200 mM urotropine, by a factor of 12–850 (Table 3, Figures 5 and 6). Addition of 0.05 M Fe(III) or 0.05 M Fe(III) +0.05–0.25 M Fe(II) to such a medium does not significantly reduce the efficiency of both inhibitors studied at $t=25\text{--}80^\circ\text{C}$. In such systems, the values of $k=0.74\text{--}2.6$ and $0.37\text{--}2.6$ $\text{g}/(\text{m}^2\cdot\text{h})$ are obtained for two- and three-component inhibitors, which is a good result. However, at $t=100^\circ\text{C}$, both inhibitors significantly lose the steel protection efficiency. If individual Fe(II) is added to 2 M H_3PO_4 , satisfactory protection of two- and three-component inhibitors persists to temperatures up to 100°C , providing $k \leq 5.9$ and 4.5 $\text{g}/(\text{m}^2\cdot\text{h})$, respectively.

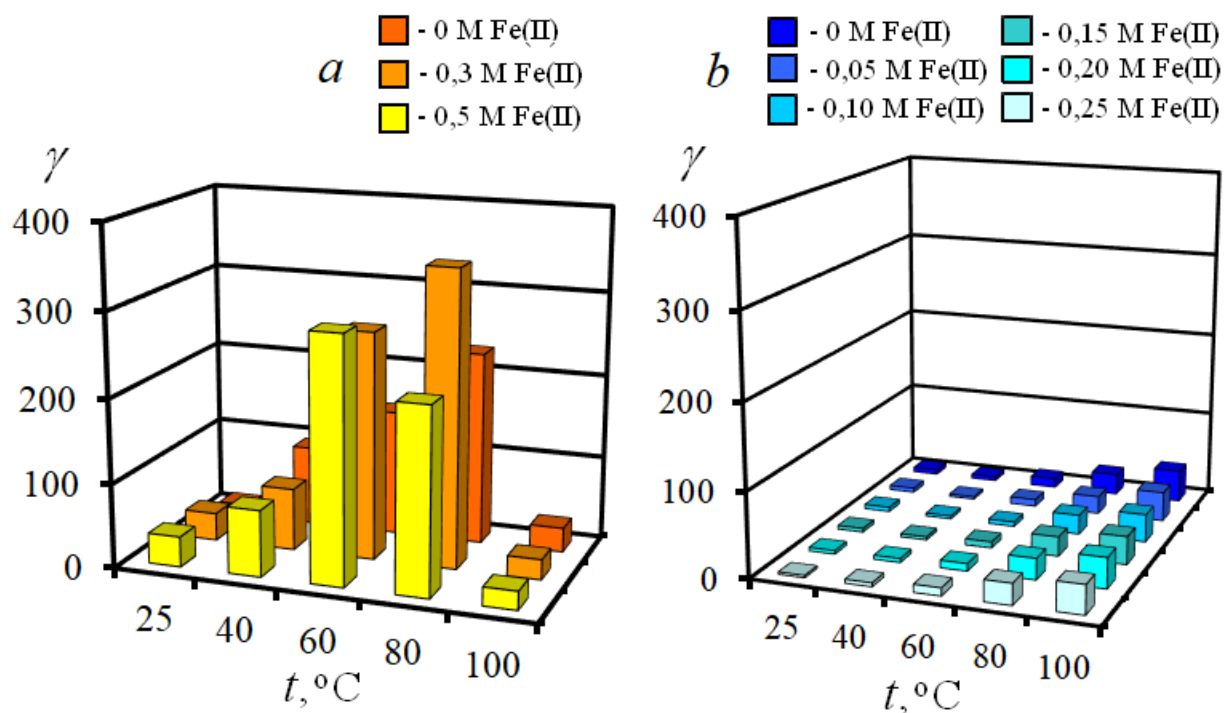


Figure 3. Corrosion inhibition coefficients of 08PS steel in 2 M H_2SO_4 (a) and 2 M $\text{H}_2\text{SO}_4 + 0.05 \text{ M Fe(III)}$ (b) with addition of 4.5 mM IFKhAN-92 + 0.5 mM KNCS in the presence of various concentrations of Fe(II) salts.

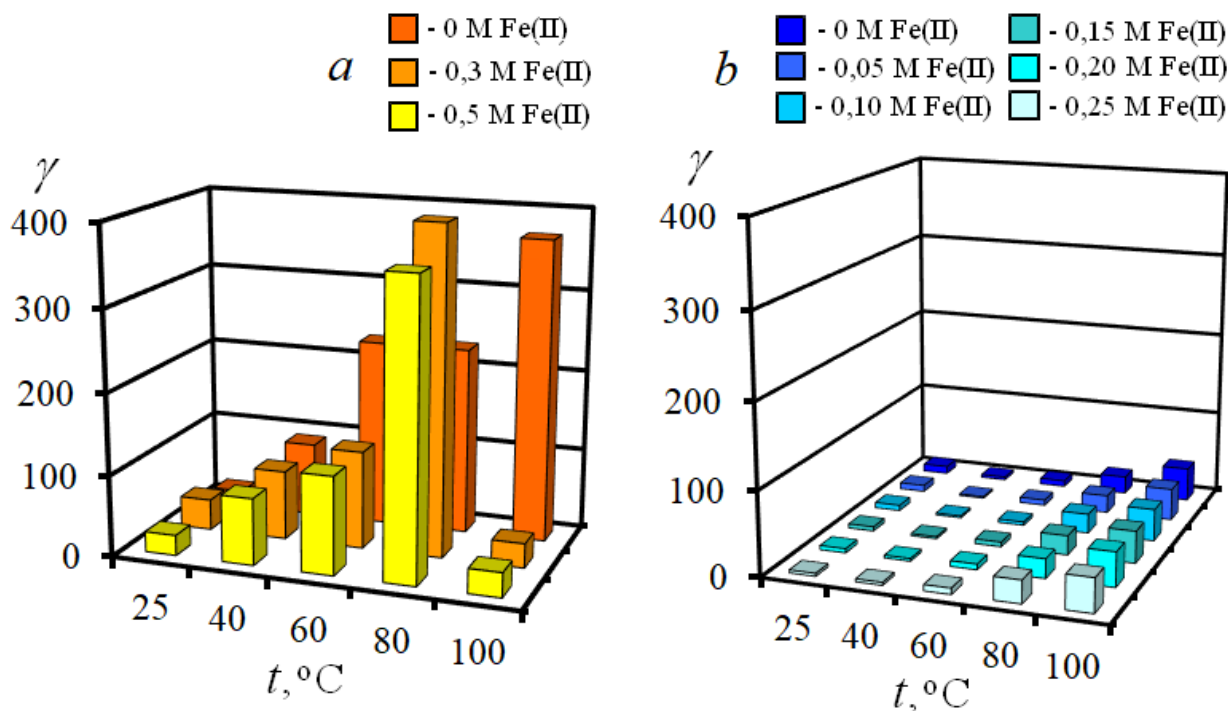


Figure 4. Corrosion inhibition coefficients of 08PS steel in 2 M H_2SO_4 (a) and 2 M $\text{H}_2\text{SO}_4 + 0.05 \text{ M Fe(III)}$ (b) with addition of 4.5 mM IFKhAN-92 + 0.5 mM KNCS + 200 mM urotropine in the presence of various concentrations of Fe(II) salts.

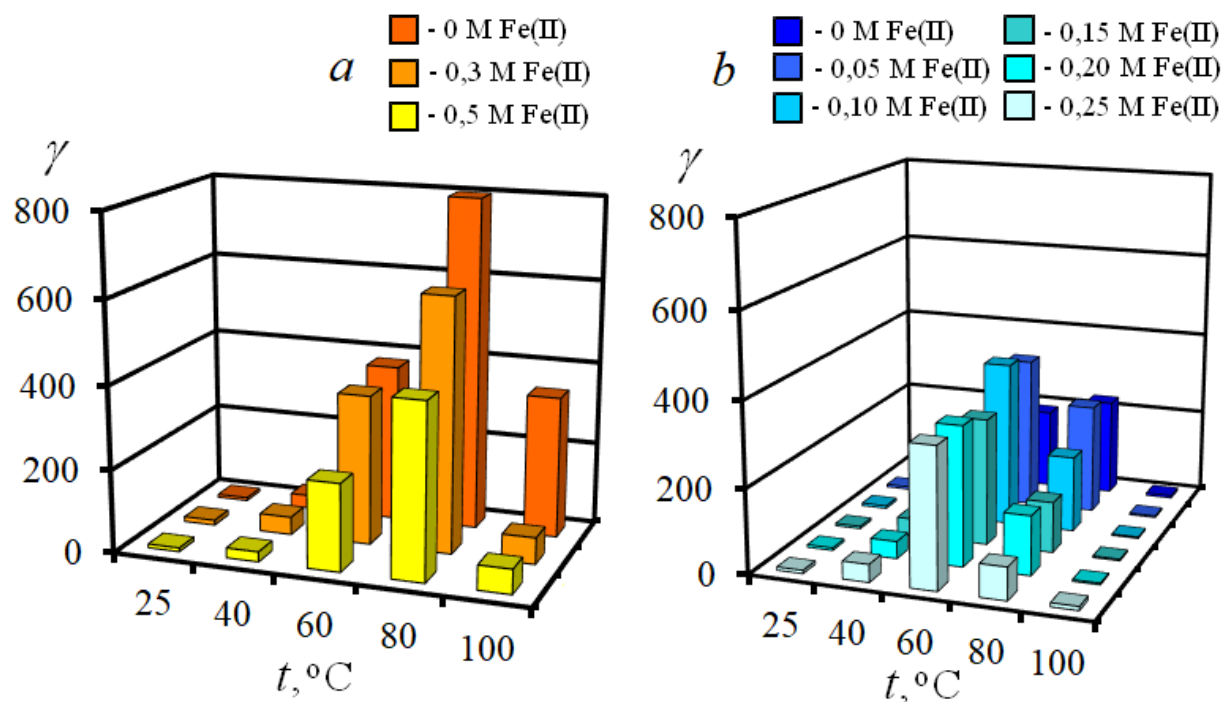


Figure 5. Corrosion inhibition coefficients of 08PS steel in 2 M H_3PO_4 (a) and 2 M $\text{H}_3\text{PO}_4 + 0.05 \text{ M Fe(III)}$ (b) with addition of 4.5 mM IFKhAN-92 + 0.5 mM KNCS in the presence of various concentrations of Fe(II) salts.

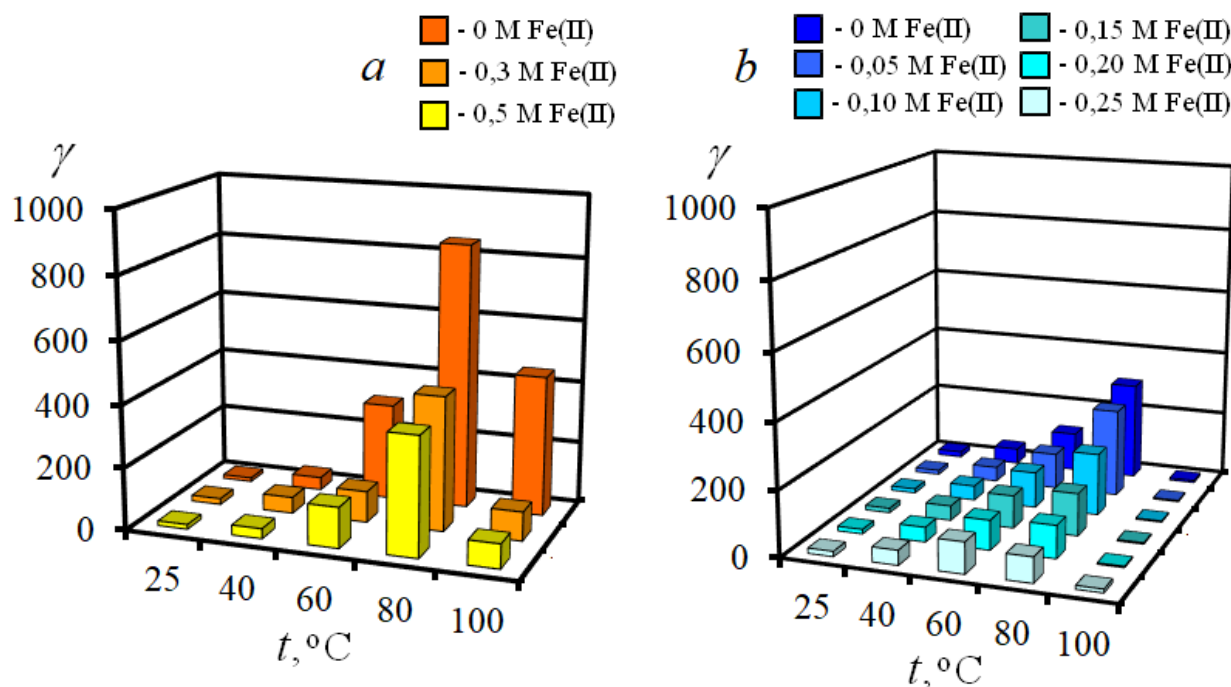


Figure 6. Corrosion inhibition coefficients of 08PS steel in 2 M H_3PO_4 (a) and 2 M $\text{H}_3\text{PO}_4 + 0.05 \text{ M Fe(III)}$ (b) with addition of 4.5 mM IFKhAN-92 + 0.5 mM KNCS + 200 mM urotropine in the presence of various concentrations of Fe(II) salts.

To summarize, the IFKhAN-92+KNCS binary mixture (molar ratio of components 9:1) and the IFKhAN-92+KNCS+urotropine three-component mixture (9:1:400) developed by us are efficient in protecting 08PS low-carbon steel in the 1 M H_2SO_4 +1 M H_3PO_4 solution in the range $t=25-100^\circ\text{C}$. These inhibitor mixtures are fairly resistant to the accumulation of high concentrations of Fe(III) and Fe(II) salts and their mixtures in 1 M H_2SO_4 +1 M H_3PO_4 . Although some corrosion acceleration is often observed in their presence in inhibited 1 M H_2SO_4 +1 M H_3PO_4 , the k values remain low, especially in comparison with the background media. For example, for the IFKhAN-92+KNCS mixture at temperatures up to 100°C in the presence of 0.05 M Fe(III), the value of k is $\leq 2.4 \text{ g}/(\text{m}^2\cdot\text{h})$; with 0.05 M Fe(III)+0.05–0.25 M Fe(II), $k\leq 4.7 \text{ g}/(\text{m}^2\cdot\text{h})$, and, in the presence of 0.30–0.50 M Fe(II), $k\leq 8.3 \text{ g}/(\text{m}^2\cdot\text{h})$. Addition of the IFKhAN-92+KNCS+urotropine mixture under the same conditions ($t=25-100^\circ\text{C}$) provides a slower rate of steel corrosion. In the presence of 0.05 M Fe(III), the k value is $\leq 2.3 \text{ g}/(\text{m}^2\cdot\text{h})$; 0.05 M Fe(III)+0.05–0.25 M Fe(II), $k\leq 4.1 \text{ g}/(\text{m}^2\cdot\text{h})$; and 0.30–0.50 M Fe(II), $k\leq 6.8 \text{ g}/(\text{m}^2\cdot\text{h})$. The results obtained are of practical importance since inhibited acid formulations for pickling and cleaning low-carbon steels have been developed that are resistant to the accumulation of Fe(III) and Fe(II) salts. An important additional advantage of the IFKhAN-92+KNCS+urotropine formulation in comparison with IFKhAN-92+KNCS is that it can be used to protect steels in acid mixtures of $\text{HCl}+\text{H}_3\text{PO}_4$ containing Fe(III) [18]. The inhibitor formulations studied efficiently protect low-carbon steel in 2 M H_3PO_4 containing Fe(II) at temperatures up to 100°C , but in 2 M H_3PO_4 containing Fe(III) or Fe(III)+Fe(II) they are only efficient at temperatures up to 80°C , which is slightly worse than for 1 M H_2SO_4 +1 M H_3PO_4 . In 2 M H_2SO_4 , the presence of Fe(III) and Fe(II) salts adversely affects the inhibition of steel corrosion in almost the entire t range studied. It is only in 1 M H_2SO_4 +1 M H_3PO_4 , even in the presence of Fe salts, that the formulations studied efficiently slow down the corrosion of low-carbon steel in a wide range of $t=25-100^\circ\text{C}$.

The mechanism of the facilitating effect of Fe(III) cations on the corrosion of steel in acid solutions is known: it is associated with their participation as an additional oxidizing agent in the cathodic reaction [19], but the reasons for the effect of Fe(II) salts on steel corrosion have not been discussed in literature. In our opinion, the effect of Fe(II) salts on the corrosion process is twofold. The presence of Fe(II) salts in acid solutions can lead to a decrease in their solubility in the surface layer near the metal where they accumulate as corrosion products. This process should slow down the anodic reaction of the metal and the general corrosion of steel. On the other hand, the presence of Fe(II) salts in acid media can increase their density. In such an environment, bubbles of hydrogen gas would be removed from the surface more easily, which would facilitate the cathodic reaction, speeding up the 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 should determine whether corrosion is hindered or accelerated. In hot acid solutions containing Fe(III) salts, a corrosion slowdown is observed, which is largely associated with

the reduction of Fe(III) salts by steel to Fe(II) salts, ultimately slowing down corrosion. It is important to note that the presence of Fe(II) salts in a solution along with Fe(III) salts should decrease 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 associated with the fact that they maintain the reduction of Fe(III) cations in these environments [19]. The effect of Fe(II) salts on inhibited acid solutions can be twofold. On the one hand, Fe(II) cations in solution can bind the components of the inhibitor mixture, hindering their adsorption on the steel surface and decreasing their efficiency. On the other hand, incorporation of Fe(II) cations into the polymolecular layer formed by molecules of the IFKhAN-92 inhibitor on a steel surface would improve the protective properties [18].

The more effective inhibitory protection of steel in acidic environments containing phosphate anions in the presence of Fe(III) salts in comparison with an individual H_2SO_4 solution is largely related to the ability of phosphate anions to form complex compounds with Fe(III) cations [20]. For example, Fe(III) phosphate complexes have a lower oxidizing ability and mobility compared to Fe(III) sulfate and aqueous complexes existing in H_2SO_4 solutions, which decreases their corrosiveness toward steel.

Conclusions

1. The IFKhAN-92+KNCS (molar ratio of components 9:1) and IFKhAN-92+KNCS+urotropine (9:1:400) composite inhibitors provide efficient protection of low-carbon steel in the 1 M H_2SO_4 +1 M H_3PO_4 solution containing Fe (III) and Fe(II) salts and their combinations. The strongest protective effects are provided by the three-component inhibitor mixture.
2. Stronger inhibition of steel corrosion by composite inhibitors based on IFKhAN-92 in H_2SO_4 + H_3PO_4 solutions containing Fe(III) salts, in comparison with similar solutions of individual H_2SO_4 , is largely due to the binding of Fe(III) cations by phosphate anions into complexes, which significantly reduces their chemical activity and, consequently, the effect on the corrosion process.
3. The results obtained are of importance for practice, since, based on a mixture of H_2SO_4 and H_3PO_4 , inhibited acid formulations for pickling and cleaning low-carbon steels that are resistant to the accumulation of Fe(III) and Fe(II) salts have been suggested.

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