Effect of the anionic composition of acidic solutions containing Fe(III) on the protection of low-carbon steel by a triazole inhibitor

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Abstract

The corrosion of low-carbon steel 08PS in 2 M HCl, 2 M H_2SO_4, and 2 M H_3PO_4 solutions as well as in their mixtures at $t = 20–80°C$ has been studied. Addition of a mixture of the IFKhAN-92 inhibitor, which is a triazole derivative, with KCNS slows down the corrosion of the low-carbon steel in these media. The presence of Fe(III) in the solutions weakens steel protection by the inhibitor formulation studied. The presence of phosphates in an acid solution decreases the adverse effect of Fe(III) as it binds Fe(III) cations into strong phosphate complexes. This effect is most distinct in H_3PO_4 and $H_2SO_4 + H_3PO_4$ solutions with high H_3PO_4 content. A mixture of IFKhAN-92 and KCNS forms a polymolecular inhibitor layer on the steel surface. This layer can efficiently slow down the reduction of Fe(III) phosphate complexes. In steel etching or in cleaning of steel equipment in acidic solutions, where Fe(III) salts are accumulated and accelerate steel corrosion, it is recommended to use solutions of H_3PO_4 or its mixtures with H_2SO_4 (at least 50%) inhibited by a formulation of IFKhAN-92 with KCNS.

Introduction

Etching of steels in solutions of mineral acids is accompanied by accumulation of Fe(III) salts in these solutions 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) cations occurs not only due to the reaction of iron with an acid:

$$Fe + 2H^+ = Fe^{2+} + H_2,$$
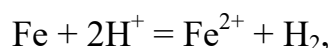
but also due to the parallel reaction of the metal with a Fe(III) salt:

$$Fe + 2Fe^{3+} = 3Fe^{2+}.$$
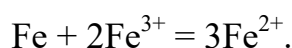
It was noted in [3] that in HCl solutions with high $FeCl_3$ content, steel corrosion predominantly occurs due to oxidation of the metal by Fe(III) cations, which may result in almost complete suppression of hydrogen evolution from the reaction of steel with HCl.

Fe(III) cations can considerably decrease the protective effect of metal corrosion inhibitors added to an etching solution [4]. It is also noted that the presence of $FeCl_3$ in inhibited hydrochloric solutions used at the plants of the oil producing complex considerably increases their corrosivity toward steel equipment [5]. Among the reasons of the decrease in inhibitor efficiency by Fe(III) cations, let us note the inhibitor removal from the corrosion medium due to its coagulation [6] and the weak inhibition of Fe(III) cathodic reduction by corrosion inhibitors, which occurs in diffusion mode [7–10].

A unique feature of the formulation of IFKhAN-92, a 3-substituted 1,2,4-triazole, with KCNS is that it can efficiently slow down the corrosion of low-carbon steel in H_3PO_4 solutions containing Fe(III) phosphate. The observed effect is based on the ability of this inhibitor formulation to strongly hinder the reduction of Fe(III) cations, along with hindrance of proton depolarization, in acidic phosphate media [11]. We believe it is important to understand whether this effect of the IFKhAN-92 + KCNS formulation is also observed in other acidic media containing Fe(III). An H_3PO_4 solution [11], HCl and H_2SO_4 solutions widely used in steel pickling [1], as well as solutions of mixtures of these acids with H_3PO_4 were used as the test media. IFKhAN-92 and its formulation with KCNS that we recommend for improvement of the protective effects of nitrogen-containing inhibitors in H_3PO_4 solutions [12, 13] were studied as steel corrosion inhibitors.

In view of the above, it is worthwhile to estimate whether it is possible to slow down the corrosion of low-carbon steel by a formulation of IFKhAN-92 with KCNS in solutions of individual acids (HCl, H_2SO_4, H_3PO_4) and their mixtures (HCl + H_3PO_4, H_2SO_4 + H_3PO_4) containing Fe(III) cations.

Experimental procedure

The corrosion rate of 08PS steel (composition, mass%: 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 2 M HCl, H_2SO_4, H_3PO_4 and HCl + H_3PO_4, H_2SO_4 + H_3PO_4 mixtures at temperatures (t) of 20–80°C was determined from the mass loss of specimens (≥3 specimens per point) sized 50 mm × 20 mm × 0.5 mm. The amount of the acid solutions was 50 ml per specimen. The test duration was 2 h. The specimens were cleaned on an abrasive disc (ISO 9001, 60 grit) and degreased with acetone prior to each experiment.

The base concentrations (C) of the individual inhibitors (IFKhAN-92 and KCNS) and their mixtures were 5.0 mM. Due to the low solubility of IFKhAN-92, it was added to the media of interest as a solution in ethanol. The resulting ethanol concentration in the pickling solution was 0.24 mol/l.

The efficiency of inhibitors was estimated from the inhibition coefficient, $\gamma = k_0/k_{in}$, where k_0 and k_{in} are the corrosion rates in the non-inhibited solution and in the solution with the compound being studied, respectively. In calculations of γ values, a solution of the

acid containing only Fe(III) cations in the corresponding concentration was used as the background solution.

In order to quantitatively estimate the effect of additivity (or synergism / antagonism) on the nitrogen-containing inhibitor, the mutual influence coefficients of the mixture components were calculated [14]:

$$K_{\mathrm{m}} = \frac{\gamma_{\mathrm{mix}}}{\prod_{i=1}^{m} \gamma_i},$$

where γ_{mix} is the corrosion inhibition coefficient for the inhibitor mixture and $\prod_{i=1}^{m} \gamma_i$ is the product of the corrosion inhibition coefficients for the individual mixture components. If $K_{\mathrm{m}} < 1$, the protection coefficients of the inhibitor components are mutually reduced; at $K_{\mathrm{m}} = 1$, an additive behavior is observed; and only at $K_{\mathrm{m}} > 1$ it should be concluded that the components of the inhibitor mixture mutually enhance the protection.

The solutions were prepared from HCl, H_3PO_4, and H_2SO_4 of "chemically pure" grade and distilled water. $FePO_4$ solutions were obtained using the reaction of excess H_3PO_4 with $Fe(OH)_3$ precipitated by NaOH ("chemically pure" grade) from a $FeCl_3$ solution. The Fe(III) chloride solution was prepared from $FeCl_3 \cdot 6H_2O$ ("pure" grade). HCl solutions containing Fe(III) chloride were prepared from $FeCl_3 \cdot 6H_2O$ ("pure" grade). H_2SO_4 solutions containing Fe(III) sulfate were prepared from $Fe_2(SO_4)_3 \cdot 9H_2O$ ("chemically pure" grade).

Experimental results and discussion

The corrosion of 08PS steel in 2 M HCl is accelerated with an increase in t. An increase in the solution temperature by 60°C increases k 240-fold (Table 1). Steel corrosion slows down at $C_{\mathrm{Fe(III)}} \leq 0.01$ M but it is accelerated at $C_{\mathrm{Fe(III)}} \geq 0.05$ M. The corrosion inhibition by low $FeCl_3$ concentrations is apparently due to the reduction of this salt to $FeCl_2$ at the metal surface. As a result, the content of $FeCl_2$ in the near-surface layer adjacent to the metal increases. The $FeCl_2$ formed due to anodic ionization of the steel is less soluble in this medium, which slows down the anodic reaction of the metal and the entire corrosion process. At higher Fe(III) contents, corrosion becomes faster due to strong acceleration of the cathodic reaction by the Fe(III) cations being reduced. At $C_{\mathrm{Fe(III)}} = 0.1$ M, the increase in k in comparison with the background solution amounted to 6.9 g/(m²·h) at 20°C and was much higher at 80°C, namely, 66 g/(m²·h). The process accelerated 3.8-fold at $t = 20$°C and only 1.1-fold at $t = 80$°C. The presence of Fe(III) cations in the HCl solution accelerates the metal corrosion, but their contribution to the overall corrosion decreases with an increase in t.

Table 1. Effect of Fe(III) cations on the corrosion rate of 08PS steel in acid solutions. Test duration: 2 h.

Solution	$C_{Fe(III)}$, M	Temperature, °C			
		20	40	60	80
2.0 M HCl	0	2.5	12	67	598
	0.005	1.9	9.4	53	564
	0.01	1.8	11	58	588
	0.02	2.5	13	63	595
	0.05	5.1	17	77	608
	0.1	9.4	22	89	664
1.0 M HCl + 1.0 M H_3PO_4	0	4.0	9.5	54	357
	0.005	3.6	7.4	50	310
	0.01	3.1	7.2	48	327
	0.02	3.9	12	52	382
	0.05	5.1	15	70	402
	0.1	8.2	18	83	445
2.0 M H_2SO_4	0	9.8	51	172	680
	0.005	10	51	172	681
	0.01	11	54	181	690
	0.02	12	56	183	699
	0.05	15	59	195	710
	0.1	18	61	204	750
1.0 M H_2SO_4 + 1.0 M H_3PO_4	0	8.5	41	143	527
	0.005	8.5	41	139	527
	0.01	8.7	42	138	515
	0.02	10	44	136	501
	0.05	11	46	131	500
	0.1	13	55	131	500
2.0 M H_3PO_4	0	7.8	28	105	439
	0.005	7.8	24	90	437
	0.01	7.8	22	87	424
	0.02	7.9	21	71	400
	0.05	8.2	23	71	371
	0.1	9.7	27	71	324

Like in 2 M HCl, the corrosion of 08PS steel in 2 M H_2SO_4 is intensified with an increase in t, but the observed k values of steel are considerably higher. An increase in the solution temperature by 60°C increases the k value 69-fold. In the entire selected t range, steel corrosion is accelerated by the presence of Fe(III) cations in the solution. They serve as an additional oxidant along with the acid. At $C_{Fe(III)} = 0.1$ M, the increase in k in comparison with the background solution amounted to 8.2 g/(m^2·h) at 20°C and was much higher, namely, 70 g/(m^2·h), at 80°C. The process accelerated 1.8- and 1.1-fold at these temperatures, respectively.

Steel corrosion in the background 2 M H_3PO_4 solution occurs with smaller k values in comparison with the H_2SO_4 solution, while at $t = 80$°C, in comparison with the HCl solution as well. An increase in t by 60°C accelerates corrosion only 56-fold. At 20–40°C, Fe(III) ions accelerate the metal corrosion at $C = 0.05–0.1$ M. However, corrosion slows down at higher temperatures at any $C_{Fe(III)}$ values. While steel corrosion acceleration by Fe(III) cations can be easily explained by their oxidizing ability, the reasons of their inhibitive effects can only be assumed. Most likely, at $t \geq 60$°C all Fe(III) cations present in the acid are rather quickly reduced to Fe(II) cations, which are accumulated in the solution. The presence of Fe(II) in the solution should decrease the solubility of Fe(II) formed on steel surface during the anodic reaction, which slows down the overall anodic process.

It should be noted that Fe(III) most strongly accelerates the corrosion of steel in acidic sulfate and chloride media. Conversely, their negative effect on corrosion is weaker in phosphate solutions, apparently due to binding of Fe(III) cations by phosphate anions into strong complexes: $[FeHPO_4]^+$, $[FeH_2PO_4]^{2+}$, and $[Fe(H_2PO_4)_4]^-$ (the instability constants are $pK_s = 9.75$; 3.5 and 9.15, respectively) [15]. They probably have weaker oxidizing ability than Fe(III) cations.

In 1 M HCl + 1 M H_3PO_4, both in the background solution and in the presence of Fe(III), the k values of 08PS steel are smaller than in 2 M HCl or 2 M H_3PO_4. The opposite effect is only observed in hot 2 M H_3PO_4 with high $C_{Fe(III)}$. Similarly to the HCl solution, steel corrosion slows down at $C_{Fe(III)} \leq 0.01$ M, but it accelerates at $C_{Fe(III)} \geq 0.05$ M.

In 1 M H_2SO_4 + 1 M H_3PO_4, the k values of 08PS steel are higher than those in 2 M H_3PO_4 but lower than in 2 M H_2SO_4. Like in phosphate solutions, at 20–40°C the Fe(III) ions accelerate the metal corrosion at $C = 0.01–0.1$ M, but at higher temperatures, the k value decreases in the entire $C_{Fe(III)}$ range.

In 2 M HCl, 2 M H_2SO_4, 2 M H_3PO_4, 1 M HCl + 1 M H_3PO_4, and 1 M H_2SO_4 + 1 M H_3PO_4 (60°C), in the absence of Fe(III), good protection can be achieved using the IFKhAN-92 + KCNS mixture (Table 2). The lowest k values for steel in 2 M H_2SO_4, 2 M H_3PO_4, and 1 M H_2SO_4 + 1 M H_3PO_4 are observed with the IFKhAN-92 + KCNS mixture with a component molar ratio of $n = 9 : 1$, which slows down corrosion 170-, 260-, and 150-fold, respectively. At all the n values studied, synergism of the action of the components is observed. It is characterized by high K_m values. In 2 M HCl, the maximum protective effect is shown by the mixture with $n = 1 : 1$, whereas in 1 M HCl + 1 M H_3PO_4,

by the mixture with $n = 4:1$. They slow down corrosion only 37- and 45-fold, respectively. The formulations are antagonistic in these media ($K_m < 1$).

Table 2*. Effect of Fe(III) cations on the corrosion rate of 08PS steel (k, g/(m^2·h)) in acid solutions containing 5.0 mM of the IFKhAN-92 + KCNS mixture. The test duration was 2 h, 60°C.

Solution	$C_{Fe(III)}$, M	$C_{IFKhAN-92}$, mM	0	0.5	1.0	2.5	4.0	4.5	4.75	5.0
		C_{KCNS}, mM	5.0	4.5	4.0	2.5	1.0	0.5	0.25	0
2.0 M HCl	0	k	36	2.0	2.0	1.8	2.4	2.6	2.8	2.5
		γ	1.9	34	34	37	28	26	24	27
		K_m	–	0.66	0.66	0.72	0.55	0.51	0.47	–
	0.05	k	41	10	9.4	9.4	9.4	9.1	9.1	9.1
		γ	1.9	7.7	8.2	8.2	8.2	8.5	8.5	8.5
		K_m	–	0.47	0.58	0.58	0.58	0.53	0.53	–
1.0 M HCl + 1.0 M H$_3$PO$_4$	0	k	18	1.3	1.3	1.3	1.2	1.5	1.6	1.9
		γ	3.0	42	42	42	45	36	34	28
		K_m	–	0.50	0.50	0.50	0.54	0.43	0.40	–
	0.05	k	33	6.2	6.2	6.0	5.9	5.3	6.0	6.2
		γ	2.1	11	11	12	12	13	12	11
		K_m	–	0.48	0.48	0.52	0.52	0.56	0.52	–
2.0 M H$_2$SO$_4$	0	k	140	1.6	1.4	1.1	1.1	1.0	1.1	13
		γ	1.2	110	120	160	160	170	160	13
		K_m	–	7.1	7.7	10	10	11	10	–
	0.05	k	180	12	7.4	5.4	5.1	5.6	5.7	16
		γ	1.1	16	26	36	38	35	34	12
		K_m	–	1.2	2.0	2.7	2.9	2.7	2.6	–
1.0 M H$_2$SO$_4$ + 1.0 M H$_3$PO$_4$	0	k	120	1.6	1.2	1.0	0.96	0.93	1.0	14
		γ	1.2	89	120	140	150	150	140	10
		K_m	–	7.4	10	12	13	13	12	–
	0.05	k	85	9.1	4.6	2.9	2.3	2.3	2.7	14
		γ	1.5	14	28	45	57	57	49	9.4
		K_m	–	0.99	2.0	3.2	4.0	4.0	3.5	–

Solution	$C_{Fe(III)}$, M	$C_{IFKhAN-92}$, mM	0	0.5	1.0	2.5	4.0	4.5	4.75	5.0
		C_{KCNS}, mM	5.0	4.5	4.0	2.5	1.0	0.5	0.25	0
2.0 M H$_3$PO$_4$	0	k	18	0.66	0.59	0.55	0.43	0.41	0.47	20
		γ	5.8	160	180	190	240	260	220	5.3
		K_m	–	5.2	5.9	6.2	7.8	8.5	7.1	–
	0.05	k	43	1.3	1.1	0.63	0.58	0.63	0.68	19
		γ	1.7	55	65	110	120	110	100	3.7
		K_m	–	8.7	10	17	19	17	16	–

* The corrosion rates in 2.0 M HCl, 1.0 M HCl + 1.0 M H$_3$PO$_4$, 2.0 M H$_2$SO$_4$, 1.0 M H$_2$SO$_4$ + 1.0 M H$_3$PO$_4$, and 2.0 M H$_3$PO$_4$ are 67, 54, 172, 143, and 105 g/(m^2·h), while those in the presence of 0.05 M Fe(III) are 77, 70, 195, 131, and 71 g/(m^2·h), respectively.

In 2 M HCl and 2 M H$_2$SO$_4$ containing 0.05 M Fe(III), the protective effect of the inhibitor formulation decreases considerably. The k of steel increases 3.3–5.2 and 4.6–7.5 fold, respectively. The K_m values decrease in these systems in comparison with the solutions containing no Fe(III). The highest protective effect in HCl is shown by the mixtures with $n \geq 9$, while in H$_2$SO$_4$, by the mixture with $n = 4$. In HCl containing Fe(III), the considerable shift of the optimum protective concentration of the IFKhAN-92 + KCNS mixture towards high $C_{IFKhAN-92}$ values in comparison with the solution without Fe(III) can be explained by binding of CNS$^-$ anions with Fe(III) into a complex. As a result, inhibition of steel corrosion is mostly provided by IFKhAN-92 molecules. Consequently, an increase in the fraction of IFKhAN-92 in the inhibitor mixture improves its protective effect.

Conversely, the presence of 0.05 M Fe(III) in 2 M H$_3$PO$_4$ enhances the synergism of the components and more weakly decreases the protective effect of the inhibitor formulation, increasing the k of steel only 1.3- to 2.0-fold. The highest protective effect is shown by the mixture with $n = 4$. An important feature of the IFKhAN-92 + KCNS mixture in 2 M H$_3$PO$_4$ is that the k of steel in the presence of Fe(III) is low ($k_{min} =$ 0.58 g/(m^2·h)).

The presence of 0.05 M Fe(III) in 1 M HCl + 1 M H$_3$PO$_4$ and 1 M H$_2$SO$_4$ + 1 M H$_3$PO$_4$ decreases the protective effect of the inhibitor formulation, increasing k of steel in the acids 3.8–4.9 and 2.5–5.7 fold, respectively. In 1 M H$_2$SO$_4$ + 1 M H$_3$PO$_4$, the synergism of action of the mixture components becomes much weaker, *i.e.*, the K_m values decrease. The corrosion of steel in 1 M HCl + 1 M H$_3$PO$_4$ is weaker than in 2 M HCl: $k =$ 5.3–6.2 and 9.1–10 g/(m^2·h), respectively. In 1 M H$_2$SO$_4$ + 1 M H$_3$PO$_4$, steel corrosion is characterized by $k_{min} = 2.3$ g/(m^2·h), which is also smaller than in 2 M H$_2$SO$_4$ where $k_{min} =$ 5.1 g/(m^2·h). Thus, replacement of a fraction of HCl or H$_2$SO$_4$ in their solutions by H$_3$PO$_4$ makes it possible to decrease the adverse effect of Fe(III) cations on the protective

properties of IFKhAN-92 + KCNS inhibitor formulations. In subsequent studies, we used the standard IFKhAN-92 + KCNS mixture with $n = 9$, which most typically provides the maximum protection in acids, both in the absence and in the presence of Fe(III).

It appears important to study the effect of temperature on the protective effect of the formulation of IFKhAN-92 with rhodanide anions in the presence of Fe(III) in the media being studied. In 2 M HCl (20–80°C), the formulation of 4.5 mM IFKhAN-92 + 0.5 mM KCNS decreases the corrosion of 08PS steel 6.8–54 fold (Table 3, Figure 1). The presence of Fe(III) cations in the solution accelerates steel corrosion considerably: in the presence of 0.1 M Fe(III), it increases 21-fold at 20°C and 2.5-fold at 80°C. In these cases, the increase in the k of steel due to the presence of Fe(III) cations in the solution amounts to 7.2 and 16 g/(m^2·h), respectively. The adverse affect of Fe(III) on the protection by the mixed inhibitor is stronger at low temperatures.
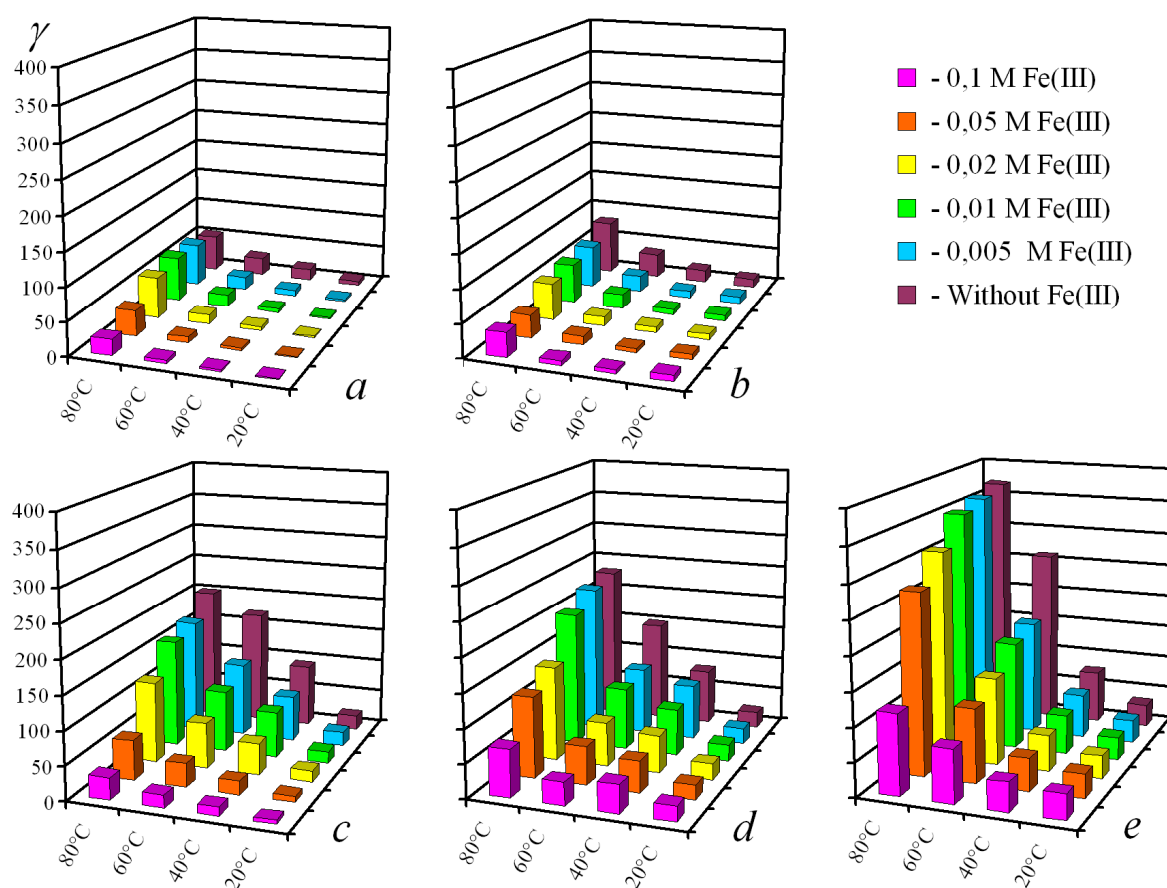
Figure 1. Effect of Fe(III) cations on the corrosion inhibition coefficients of 08PS steel in 2 M HCl (*a*), 1 M HCl + 1 M H$_3$PO$_4$ (*b*), 2 M H$_2$SO$_4$ (*c*), 1 M H$_2$SO$_4$ + 1 M H$_3$PO$_4$ (*d*), and 2 M H$_3$PO$_4$ (*e*) containing 4.5 mM IFKhAN-92 + 0.5 mM KCNS. Test duration: 2 h.

Table 3. Effect of Fe(III) cations on the corrosion rate of 08PS steel (k, g/(m$^2\cdot$h)) in acid solutions containing 4.5 mM of the IFKhAN-92 + 0.5 mM KCNS mixture. Test duration: 2 h.

Solution	$C_{Fe(III)}$, M	Temperature, °C			
		20	40	60	80
2.0 M HCl	0	0.37	0.70	2.6	11
	0.005	0.60	1.1	2.6	9.0
	0.01	0.92	2.0	3.2	8.8
	0.02	1.3	2.3	4.6	9.7
	0.05	3.8	5.1	9.1	16
	0.1	7.6	9.7	17	27
1.0 M HCl + 1.0 M H$_3$PO$_4$	0	0.30	0.50	1.5	4.4
	0.005	0.32	0.73	2.0	4.9
	0.01	0.38	0.88	2.3	5.5
	0.02	0.49	1.4	3.6	6.9
	0.05	0.66	2.8	5.3	12
	0.1	0.92	3.4	11	21
2.0 M H$_2$SO$_4$	0	0.46	0.55	1.0	3.4
	0.005	0.48	0.75	1.5	4.1
	0.01	0.66	0.79	2.0	4.3
	0.02	0.76	1.2	2.7	5.9
	0.05	1.9	3.0	5.6	12
	0.1	3.5	4.7	11	23
1.0 M H$_2$SO$_4$ + 1.0 M H$_3$PO$_4$	0	0.35	0.50	0.93	2.3
	0.005	0.35	0.50	1.4	2.4
	0.01	0.35	0.61	1.5	2.6
	0.02	0.41	0.78	2.1	3.6
	0.05	0.50	1.0	2.3	4.2
	0.1	0.56	1.3	3.9	7.0
2.0 M H$_3$PO$_4$	0	0.23	0.36	0.41	1.2
	0.005	0.23	0.37	0.53	1.2
	0.01	0.23	0.38	0.55	1.2
	0.02	0.23	0.39	0.57	1.3
	0.05	0.23	0.48	0.63	1.4
	0.1	0.26	0.63	0.90	2.8

An essentially different behavior is observed in 2 M H_3PO_4 + 4.5 mM IFKhAN-92 + 0.5 mM KCNS where the adverse effect of Fe(III) salts on the corrosion process is very weak. The corrosion in the presence of 0.1 M Fe(III) is accelerated only 1.1-fold at 20°C and 2.3-fold at 80°C. Here the increase in the k of steel due to the presence of Fe(III) cations in the solution amounts to 0.03 and 1.6 g/(m²·h), respectively.

In protection of 08PS steel by a mixture of 4.5 mM IFKhAN-92 + 0.5 mM KCNS in 1 M HCl + 1 M H_3PO_4 in the presence of Fe(III), in all the cases the metal corrosion is characterized by smaller k values than in a similar situation in 2 M HCl. As a consequence, the adverse effect of Fe(III) salts on the protective effect of the inhibitor is weaker, especially at $t \leq 40$°C where $k \leq 3.4$ g/(m²·h). Under the same conditions in 2 M HCl, $k \leq 9.7$ g/(m²·h). Corrosion in the presence of 0.1 M Fe(III) is accelerated 3.1-fold at 20°C and 4.8-fold at 80°C. The increase in the k of steel due to the presence of Fe(III) cations in the solution amounts to 0.62 and 17 g/(m²·h), respectively.

In 2 M H_2SO_4 (20–80°C), the formulation of 4.5 mM IFKhAN-92 + 0.5 mM KCNS slows down the corrosion of 08PS steel 21–200 fold, which characterizes it as a very efficient inhibitor, but the presence of the Fe(III) salt in the acid solution increases the k of the metal considerably. The presence of 0.1 M Fe(III) accelerates corrosion 7.6-fold at 20°C and 6.8-fold at 80°C, while the increase in the k of the steel amounts to 3.0 and 20 g/(m²·h), respectively.

An interesting result is observed in 1 M H_2SO_4 + 1 M H_3PO_4 + 4.5 mM IFKhAN-92 + 0.5 mM KCNS, where the Fe(III) cations increase the steel corrosion much more weakly than in pure H_2SO_4. Corrosion in the presence of 0.1 M Fe(III) is accelerated 1.6-fold at 20°C and 3.0-fold at 80°C. In this case, the increase in the k of steel due to the presence of Fe(III) in the solution amounts to 0.21 and 4.7 g/(m²·h), respectively. In this medium inhibited by 4.5 mM IFKhAN-92 + 0.5 mM KCNS, the maximum k at $t \leq 80$°C amounts to 7.0 g/(m²·h). From a practical standpoint, the best protection of the steel in this mixture of acids is achieved either at a low content of Fe(III) salts or at relatively low temperatures ($t \leq 40$°C). For example, at $t \leq 40$°C and $C_{Fe(III)} \leq 0.1$ M, $k \leq 1.3$ g/(m²·h).

The protective effect of the inhibitor formulation being studied strongly depends on the anionic composition of the corrosive medium. In the H_2SO_4 + H_3PO_4 mixture with a total acid concentration of 2 M containing 0.05 M Fe(III), corrosion of the steel slows down as the H_3PO_4 content in the mixture increases (Figure 2). In solutions containing up to 25% H_3PO_4, the k values of 08PS steel are close to that in 2 M H_2SO_4 + 0.05 M Fe(III). An increase in the H_3PO_4 content from 25 to 40% slows down steel corrosion abruptly, after which k decreases monotonously until the content of H_3PO_4 is 97.5%, and then again decreases abruptly to the value corresponding to 2M H_3PO_4 + 0.05 M Fe(III).

Addition of the 4.5 mM IFKhAN-92 + 0.5 mM KCNS mixture to these media decreases k 36- to 190-fold (Figure 3). The corrosion rate of steel in solutions containing up to 40% H_3PO_4 and this inhibitor mixture is comparable to the k of steel observed in 2 M H_2SO_4 + 0.05 M Fe(III) + 4.5 mM IFKhAN-92 + 0.5 mM KCNS, while at molar fractions $\chi_{H3PO4} \geq 75$%, it is comparable to the k of steel in 2 M H_3PO_4 + 0.05 M Fe(III) + 4.5 mM

IFKhAN-92 + 0.5 mM KCNS. As a result, at $\chi_{H3PO4} \geq 75\%$, the γ for the inhibitor mixture is > 100.
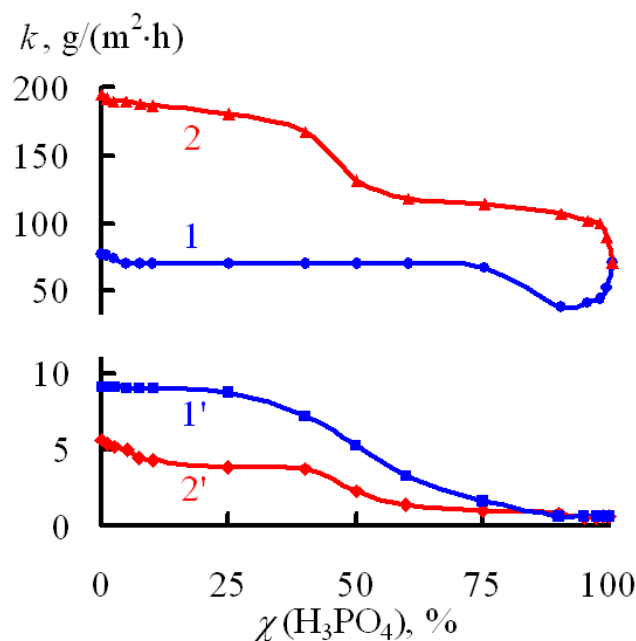
Figure 2. Corrosion rates of 08PS steel in 2 M HCl + H_3PO_4 (*1, 1′*) and 2 M H_2SO_4 + H_3PO_4 (*2, 2′*) with addition of 0.05 M Fe(III) containing 4.5 mM IFKhAN-92 + 0.5 mM KCNS (*1′, 2′*) at various H_3PO_4 molar fractions. The test duration was 2 h, $t = 60°C$.
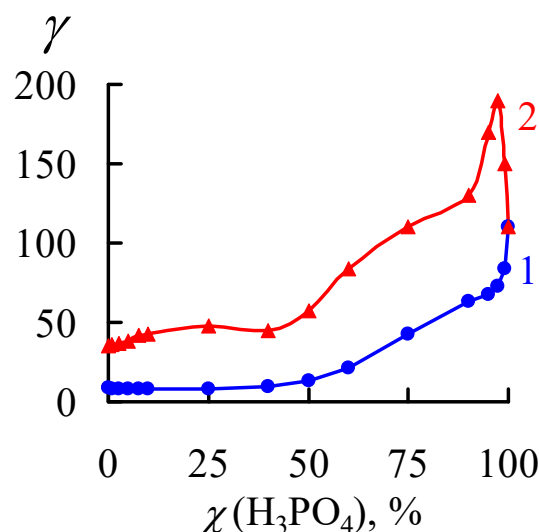
Figure 3. Corrosion inhibition coefficients of 08PS steel in 2 M HCl + H_3PO_4 (1) and 2 M H_2SO_4 + H_3PO_4 (2) with addition of 0.05 M Fe(III) containing 4.5 mM IFKhAN-92 + 0.5 mM KCNS at various H_3PO_4 molar fractions. The test duration was 2 h, $t = 60°C$.

In the HCl + H_3PO_4 mixture with a total acid concentration of 2 M containing 0.05 M Fe(III), steel corrosion in solutions with $\chi_{H3PO4} \leq 75\%$ occurs with k values close to those

in 2 M HCl (Figure 2). A further increase in the H_3PO_4 content in the mixture decreases the k of steel abruptly. The minimum steel corrosion is observed in the solution with $\chi_{H3PO4} = 90\%$. In solutions with $\chi_{H3PO4} > 90\%$, corrosion increases with an increase in the H_3PO_4 content, approaching the k values of steel observed in 2 M H_3PO_4. Addition of 4.5 mM IFKhAN-92 + 0.5 mM KCNS to these media decreases k just 7.8- to 84-fold, while $\gamma > 10$ is observed at $\chi_{H3PO4} \geq 50\%$ (Figure 3). In chloride-phosphate mixtures containing Fe(III), the inhibitor mixture appears much less efficient than in sulfate-phosphate media.

The explanation for the differences in the behavior of the IFKhAN-92 + KCNS inhibitor formulation in Fe(III)-containing HCl + H_3PO_4 and H_2SO_4 + H_3PO_4 solutions lies in the specifics of the mechanism of action of this inhibitor and in the chemical properties of the anions in the corrosive medium. Chloride anions have the lowest complexing ability with respect to Fe(III) cations: $pK_н([FeCl]^{2+}) = 1.45$, $pK_н([FeCl_2]^+) = 2.10$, $pK_н([FeCl_3]) = 1.10$, $pK_н([FeCl_4]^-) = -0.85$. Sulfate complexes of Fe(III) are more stable: $pK_н([FeSO_4]^+) = 4.18$, $pK_н([Fe(SO_4)_2]^-) = 7.4$. Phosphate anions form the strongest complexes with Fe(III): $pK_н[FeHPO_4]^+) = 9.75$, $pK_н([FeH_2PO_4]^{2+}) = 3.5$, $pK_н([Fe(H_2PO_4)_4]^-) = 9.15$ [15]. In inhibited solutions, metallic iron is most easily oxidized by non-complexed Fe(III) ions. The lower their concentration in a solution, the smaller the adverse effect of Fe(III) on the corrosion process. Based on the instability constants of Fe(III) chloride and sulfate complexes, the content of free Fe(III) cations is high in HCl and H_2SO_4 solutions, and as a result, the inhibitor formulation poorly protects the steel. The content of free Fe(III) cations in H_3PO_4 solutions should be minimal. As a result, the inhibitor mixture efficiently hinders corrosion in phosphate solutions. Judging by the instability constants of Fe(III) complexes, the anions in sulfate-phosphate solutions should be more liable to complexation in comparison to those in chloride-phosphate media. As a result, the IFKhAN-92 + KCNS inhibitor formulation is efficient in H_2SO_4 + H_3PO_4 solutions with high H_3PO_4 content.

The IFKhAN-92 + KCNS formulation forms a chemisorbed polymolecular layer on the steel surface being protected. The layer consists of triazole molecules, rhodanide anions and Fe(II) cations bound by donor-acceptor interactions [16]. This layer rather successfully prevents the reduction of complex Fe(III) ions, primarily phosphate ones, on the steel surface, thus preventing the metal corrosion. This is indicated by our earlier data on the cathodic reduction of Fe(III) cations on steel in acidic phosphate solutions [11].

Thus, in order to prevent the adverse corrosion effect of Fe(III) salts, which accumulate in various acidic formulations used in scale pickling and in washing of process equipment, on steel items and equipment, it can be recommended to use H_3PO_4 solutions inhibited with the IFKhAN-92 + KCNS formulation for these operations under industrial conditions. To reduce the cost of this solution, a fraction of H_3PO_4 (at least 50%) can be replaced by the cheaper H_2SO_4, which will not result in a considerable loss of the inhibitor protective effect, particularly in weakly heated solutions ($t \leq 40°C$) and at relatively low Fe(III) concentrations.

Conclusions

1. The acid solutions studied can be arranged in the following sequence in terms of to their corrosivity toward 08PS steel in the range of $t = 20-80°C$: 2 M H_2SO_4 > 1 M H_2SO_4 + 1 M H_3PO_4 > 2 M H_3PO_4 > 2 M HCl > 1 M HCl + 1 M H_3PO_4. However, this sequence can be violated in the presence of high Fe(III) concentrations in H_3PO_4, HCl and HCl + H_3PO_4 solutions with $t = 60-80°C$. Fe(III) cations in 2 M H_2SO_4 considerably enhance steel corrosion. Only hindrance of steel corrosion is observed in 2 M HCl and 1 M HCl + 1 M H_3PO_4 at $C_{Fe(III)} \le 0.01$ M, but at $C_{Fe(III)} \ge 0.05$ M it accelerates, while Fe(III) cations accelerate corrosion in 2 M H_3PO_4 and 1 M H_2SO_4 + 1 M H_3PO_4 at $t \le 40°C$ but slow it down at $t \ge 60°C$.

2. The mixture of IFKhAN-92 with KCNS inhibits the corrosion of low-carbon steel in HCl, H_2SO_4, H_3PO_4, HCl + H_3PO_4, and H_2SO_4 + H_3PO_4 solutions. It has the smallest protective effect in the HCl solution, while the highest effect is observed in the H_3PO_4 solution.

3. The presence of Fe(III) cations impairs steel protection by the IFKhAN-92 + KCNS formulation in solutions of mineral acids and in their mixtures. The presence of phosphate anions decreases the adverse effect of Fe(III) on steel protection by mixed inhibitors as these anions bind Fe(III) cations into strong phosphate complexes. A mixture of IFKhAN-92 and KCNS forms a chemisorbed polymolecular inhibitor layer on a steel surface. This layer can efficiently slow down the reduction of Fe(III) phosphate complexes. This effect is most distinct in H_3PO_4 and H_2SO_4 + H_3PO_4 solutions with high H_3PO_4 content.

4. In pickling of steels or acid cleaning of steel equipment, if Fe(III) salts that accelerate the metal corrosion can potentially be accumulated in these media, it is recommended to use solutions of H_3PO_4 or its mixtures with H_2SO_4 inhibited by the IFKhAN-92 + KCNS formulation, since steel corrosion due to its reaction with Fe(III) compounds is minimized in these solutions.

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