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INHIBITOR PROTECTION OF LOW CARBON STEEL IN THE FLOW OF SULFURIC ACID SOLUTION CONTAINING IRON(III) SULFATE

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Abstract. Corrosion of low-carbon steel in the flow of H_2SO_4 solutions containing $Fe_2(SO_4)_3$, including media with additives of corrosion inhibitors, viz. catamine AB (a mixture of quaternary ammonium salts) and IFKhAN-92 (3-substituted derivative of 1,2,3-triazole) is studied. In the discussed medium, partial reactions of anodic ionization of iron, cathodic reduction of H^+ and Fe(III) cations are realized on steel. The first two reactions are characterized by kinetic control, and the latter is characterized by diffusion control. The accelerating effect of $Fe_2(SO_4)_3$ on the corrosion of steel in H_2SO_4 solution is mainly due to the reduction of Fe(III). In contrast, in an inhibited acid, the accelerating effect of Fe(III) cations affects all partial reactions of steel. The data on corrosion of low-carbon steel in the flow of the studied media obtained by mass loss of metal samples are in satisfactory agreement with the results of the study of partial electrode reactions. The accelerating effect of $Fe_2(SO_4)_3$ on steel corrosion in the flow of H_2SO_4 solutions, including in the presence of inhibitors, is noted. In these media, steel corrosion is determined by the convective factor, which is characteristic of diffusion-controlled processes. Unlike catamine AB, the IFKhAN-92 inhibitor ensures a significant slowdown of steel corrosion in the flow of H_2SO_4 solution containing $Fe_2(SO_4)_3$. The reason of higher inhibitor effects of IFKhAN-92 at protection of steel in the considered media as compared to catamine AB is that it slows down partial electrode reactions of metal more substantially.

Keywords: *convection, diffusion kinetics, acid corrosion, low-carbon steel, sulfuric acid, iron (III) sulfate, corrosion inhibitors*

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Acid solutions are widely used at various enterprises of modern production as liquids for various technological purposes [1–4]. In particular, they are used to clean steel equipment from corrosion products represented primarily by rust and from other mineral deposits. As a result of dissolution of oxide and hydroxide phases of Fe(III), such solutions are contaminated with soluble Fe(III) compounds that significantly change their properties. Accumulation of soluble Fe(III) salts in these media significantly increases their oxidizing ability, increasing the aggressiveness of solutions with respect to steel structures, and makes the use of corrosion inhibitors (CI) in such solutions ineffective. A specific feature of steel corrosion in acid solutions containing Fe(III) salts is their sensitivity to hydrodynamic parameters of the medium. In acid solutions, including inhibited media, the corrosion of steel increases with the increase in the flow rate of the medium [5].

The practical significance of the presented research is determined by the need to create effective CI of low-carbon steels in acid solutions on the basis of nitrogen-containing organic substances for the needs of modern production [6]. It is important to understand how the developed CI will protect steel in the flow of corrosive medium when Fe(III) salts accumulate in it.

To understand the processes occurring in the systems of low-carbon steel / acid solution containing Fe(III) salt, it is important to analyze the influence of the convection conditions of the corrosive medium, both on the individual stages and on the corrosion of steel as a whole. The influence of CI on the kinetic parameters of the system should be established. Assessment of the influence of hydrodynamic parameters of acid solutions containing Fe(III) salts on steel corrosion is important not only in the theoretical terms, which allows us to identify the diffusion stages of the corrosion process and determine their kinetic parameters, but also in the practical one, since industrial operation of these media is often carried out under conditions of the liquid flow or accompanied by significant natural convection as a result of release of gaseous hydrogen on the metal surface.

As a model medium for research, we chose sulfuric acid solution containing Fe(III) sulfate, which is determined by its industrial demand [7, 8]. As retarders of steel corrosion, we studied the products often used as the basis of mixed CI, viz. catamine AB (a mixture of quaternary ammonium salts (QAS)) and IFKhAN-92 (3-substituted 1,2,4-triazole). Comparative studies of these CI show that under similar conditions IFKhAN-92 has a stronger inhibition of acid corrosion of steels, which is due to polymolecular protective layers formed by this compound on the metal surface [9].

Corrosion of low-carbon steels in solutions of mineral acids (so-called "non-oxidizing agents") in a simplified form is described by the total reaction

$$2H^+ + Fe = Fe^{2+} + \acute{K}_2, \qquad (1)$$

which is the result of preferential partial reactions [10, 11]: cathodic release of hydrogen

$$2H^+ + 2e = \acute{K}_2, \qquad (2)$$

and anodic dissolution of iron

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

The peculiarities of the mechanism of reaction (2) realized on the surface of steels in acid solutions are discussed in [10–12]. The mechanisms of reaction (3) were studied by Heusler [10], Bockris [13], Kolotyrkin and Florianovich [14]. Kolotyrkin and Florianovich showed that the anodic reaction of iron in H_2SO_4 solutions proceeds with the participation of sulfate/hydrosulfate anions.

In our studies, we showed [5] that in solutions of acids containing Fe(III) salts, corrosion of low-carbon steels is realized by three independent partial reactions, viz. anodic ionization of iron (3), cathodic release of hydrogen (2), and reduction of Fe(III) cations

$$Fe^{3+} + e = Fe^{2+}. \qquad (4)$$

In solutions with high mineral acid content, partial reactions (2) and (3) are realized with kinetic control while reaction (4) is realized with diffusion control.

In our study, we believe it is reasonable to search — among corrosion retarders of various nature (QAS and triazole derivative) — for a substance effectively inhibiting partial reactions of steel (2)–(4) in acid solutions containing Fe(III) salts. We believe that such a substance should provide significant retardation of steel corrosion both in static and dynamic corrosive environments.

EXPERIMENTAL PART

Objects and Methods of Research

We used H_2SO_4 (c. p.), $Fe_2(SO_4)_3 \times 9H_2O$ (c. p.), $FeSO_4 \times 7H_2O$ (c. p.), and distilled water to prepare the solutions. We studied CI Catamine AB, which is a mixture of alkylbenzyldimethylammonium chlorides $[C_nH_{2n+1}N^+(CH_3)_2CH_2C_6H_5]Cl^-$, where $n = 10–18$, and IFKhAN-92, which is a 3-substituted 1,2,4-triazole.

We performed electrochemical measurements on low-carbon steel St3 (composition, in % by mass: C 0.14–0.22, P 0.04, Si 0.15–0.33, Mn 0.40–0.65, S 0.05, Cr 0.3, Ni 0.3, N 0.008, Cu 0.3, As 0.08, the rest is Fe) on a rotating disk electrode ($n = 460$ rpm) in hydrogen deaerated 2 M H_2SO_4 at t = 25°C. The glass electrochemical cell was thermostated using a LOIP LT-411a circulating thermostat (produced by ZAO "Laboratory Equipment and Instruments", Russia). Steel potentials were measured relative to a silver chloride electrode filled with a saturated KCl solution. The steel electrode was cleaned with M20 sandpaper and degreased with acetone. The polarization curves were recorded using an EL-02.061 potentiostat (produced by ELNITEKS, Russia) in potentiodynamic mode at a polarization rate of 0.0005 V/s. Before polarization, the electrode was kept in the solution under study for 30 min to establish the potential of free corrosion $E_{\rm cor}$, and then the curves of anodic and cathodic polarization of steel were recorded. After this, the dependence of cathodic current at $E = -0.30$ V on the electrode rotation speed ($n = 0, 460, 780, 1090, 1400$ rpm) was studied. 30 min before and during the experiments, the studied solutions were deaerated with hydrogen produced in the electrolyzer from NaOH solution. The influence of inhibitors on electrode processes was evaluated by the values of the inhibition coefficient of the cathodic reaction

$$\gamma_c = i_{\rm c,0} i_{\rm c,in}^{-1}, \qquad (5)$$

and anodic reaction

$$\gamma_a = i_{\rm a,0} i_{\rm a,in}^{-1}, \qquad (6)$$

where $i_{\rm c,0}$ and $i_{\rm a,0}$ are the densities of cathodic and anodic currents in the background solution, $i_{\rm c}$, in and $i_{\rm a}$, in are the densities of cathodic and anodic currents in the solution with the studied additive at potentials of −0.30 and −0.05 V, respectively. When calculating the values $\gamma_{\rm c}$ and $\gamma_{\rm a}$, a solution containing only Fe(III) cations of the respective concentration as additives was taken as a background one.

The values of electrode potentials are given here on the standard hydrogen scale.

The corrosion rate of 08ps steel (composition, in % by 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, the rest is Fe) in 2 M H_2SO_4 at temperature t = 20 ± 2°C was determined by mass loss of samples (not less than five per point)

$$k = \Delta m S^{-1} \tau^{-1}, \tag{7}$$

Δm is the mass change of the sample, g; S is the sample area, m^2, and τ is the duration of corrosion tests, h. The sample size is 50 mm × 20 mm × 0.5 mm. The mass of steel samples before and after corrosion tests was measured using GR-202 analytical scales (produced by AND, Japan). The volume of corrosion medium was determined at the rate of 50 ml of acid solution per sample. The duration of tests is 2 h. The studies were carried out both in static and dynamic corrosion medium at the rotation speed of propeller magnetic stirrer $n = 0$, 250, 420, 750, and 1080 rpm. The corrosion medium was stirred by an MSH-300 magnetic stirrer (produced by BioSan, Latvia). Before the experiment, the samples were cleaned on an abrasive wheel (ISO 9001, grain size 60) and degreased with acetone.

The effectiveness of inhibitors was evaluated by the values of inhibition coefficients

$$\gamma = k_0 k_{\text{in}}^{-1}, \tag{8}$$

where k_0 and k_{in} are the corrosion rates of 08ps steel in the background solution and in the solution with the studied additive. When calculating the values γ, the solution containing only Fe(III) cations of the respective concentration as additives was taken as a background solution.

The influence of the presence of dissolved Fe(III) salt in the acid, given the same rate of solution flow, and the nature of corrosion medium flow, given the constant Fe(III) content, on the corrosion rate of steel was estimated by the values of incremental corrosion losses

$$\begin{gathered} \Delta k_{\text{Fe(III)}} = k_{\text{Fe(III)}} - k_0, \\ \Delta k_{\text{dyn}} = k_{\text{dyn}} - k_{\text{st}}, \end{gathered} \tag{9}$$

and the corrosion acceleration coefficient

$$\begin{gathered} \gamma_{\text{Fe(III)}}^{-1} = k_{\text{Fe(III)}}\, k_0^{-1}, \\ \gamma_{\text{dyn}}^{-1} = k_{\text{dyn}}\, k_{\text{st}}^{-1}, \end{gathered} \tag{10}$$

where $k_{\text{Fe(III)}}$ and k_0 are the corrosion rates of 08ps steel in the acid solution in the presence and absence of Fe(III) salt, and k_{dyn} and k_{st} are the corrosion rates of the same steel in the dynamic and static environments.

The measurements were carried out using the equipment of the Center for Collective Use of Physical Research Methods of the Institute of Physical Chemistry and Electrochemistry of the Russian Academy of Sciences.

DISCUSSION OF RESULTS

Important information on the mechanism of steel corrosion in an acid solution containing Fe(III) salt can be obtained by studying the kinetics of electrode reactions of metal by voltammetry [15]. In 2 M H_2SO_4, the form of polarization curves (PC) of low-carbon steel is characteristic of corrosion occurring in the region of its active dissolution potentials (Fig. 1, Table 1). The presence of $Fe_2(SO_4)_3$ in the acid solution shifts the free corrosion potential of steel (E_{cor}) to the region of more positive potentials, which is the result of acceleration of the cathodic reaction by this additive. Fe(III) cations have almost no effect on the anodic process. A positive order of the steel cathodic reaction in terms of Fe(III) cations concentration is observed. The initial section of the cathodic PC is characterized by the limiting current (i_{lim}). On the contrary, the slope of anodic polarization corresponds to the background value.

The presence of $Fe_2(SO_4)_3$ additives in the H_2SO_4 solution practically does not affect the character of the anodic reaction, which, both in the absence and in the presence of Fe(III) sulfate, proceeds in accordance with the reaction equation (3). The character of cathodic PC indicates the participation of Fe(III) in the cathodic reaction. In concentrated acid solutions (pH < 2), the cathodic reaction corresponding to Eq. (2) proceeds in the region of kinetic control [16], which is confirmed by the character of cathodic PC we obtained. In environments containing $Fe_2(SO_4)_3$, they are complicated by the limiting current. The mechanism of the cathodic reaction changes. The observed i_{lim} is determined by diffusion limitations associated with the depolarizing agent, Fe^{3+}, present in the acid solution, being delivered to the steel surface.

We found [5] that in the region of cathodic potentials on steel in mineral acid solutions containing Fe(III) salts, independent reactions of H^+ and Fe^{3+} reduction described by Eqs. (2) and (4) are realized, and the cathodic current is composed of two partial currents. The cathodic process defined by reaction (2) occurring in the kinetic region and reaction (4) controlled by diffusion is described by the equation

$$i_{\text{c}} = i_{\text{k}} + i_{\text{d}}, \tag{11}$$

where i_{k} and i_{d} are the densities of kinetic and diffusion currents. Eectrochemical reactions proceeding with diffusion limitations are usually studied using a rotating

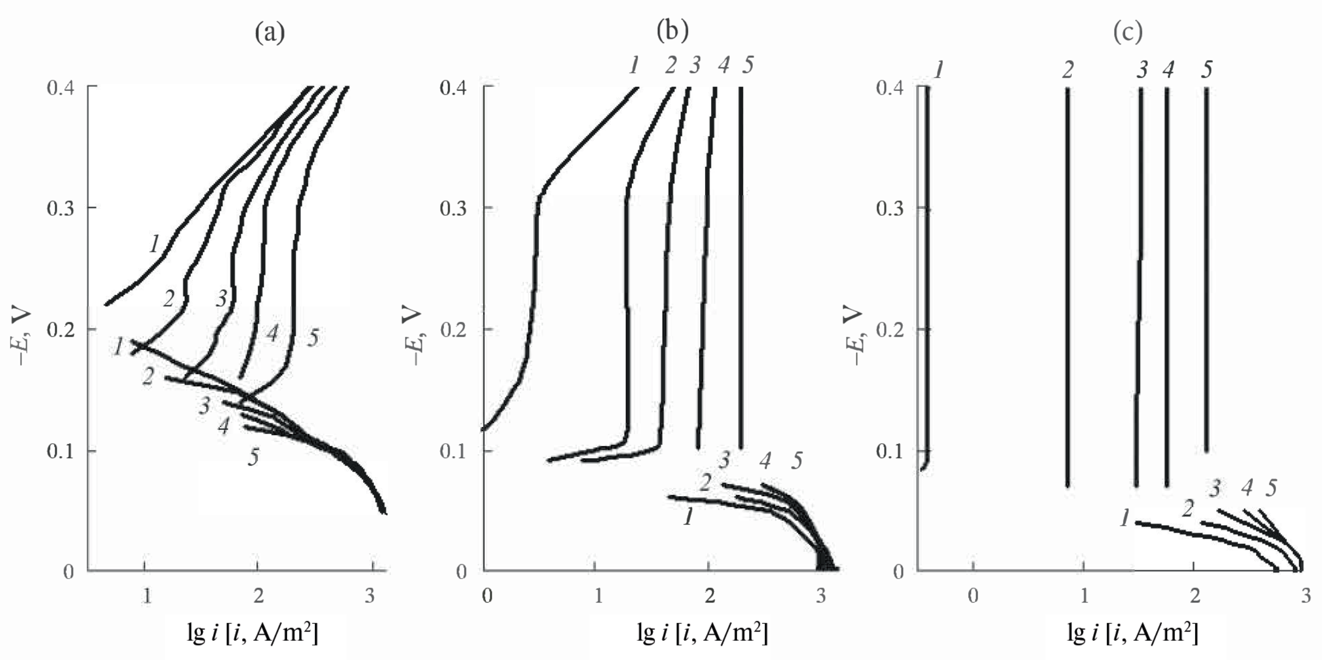

Fig. 1. Polarization curves of the St3 steel disk in 2 M H_2SO_4 (a), inhibited by 10 mM catamine AB (b) and 10 mM IFKhAN-92 (c), in the presence of Fe(III) (mol/l): (1) 0, (2) 0.02, (3) 0.05, (4) 0.10, (5) 0.20, n = 460 rpm.

Table 1. Values of corrosion potentials (E_{cor}) of St3 steel, Tafel slopes of polarization curves (b_c and b_a), cathodic and anodic current densities (i_c and i_a) and cathodic and anodic reaction inhibition coefficients (γ_c and γ_a) for $E = -0.30$ and −0.05 V, respectively. E is given in V, i is given in A/m^2, and n = 460 rpm, t = 25°C

$C_{Fe(III)}$, M	E_{cor}	b_c	i_c	γ_c	b_a	i_a	γ_a
			No inhibitor				
0	−0.20	0.10	29.2	–	0.07	1260	–
0.02	−0.17	i_{lim}*	46.2	–	0.07	1270	–
0.05	−0.15	i_{lim}	77.9	–	0.07	1340	–
0.10	−0.14	i_{lim}	119	–	0.07	1340	–
0.20	−0.13	i_{lim}	231	–	0.07	1350	–
			10 mM catamine AB				
0	−0.09	i_{lim}	3.1	9.4	0.07	292	4.3
0.02	−0.07	i_{lim}	19.2	2.4	0.07	476	2.7
0.05	−0.08	i_{lim}	46.2	1.7	0.07	615	2.2
0.10	−0.08	i_{lim}	100	1.2	0.07	692	1.9
0.20	−0.08	i_{lim}	200	1.2	0.07	692	1.9
			10 mM IFKhAN-92				
0	−0.05	i_{lim}	0.4	73.0	0.04	10**	126.0
0.02	−0.05	i_{lim}	7.3	6.3	0.04	50**	25.4
0.05	−0.06	i_{lim}	33.8	2.3	0.05	173	7.7
0.10	−0.06	i_{lim}	57.7	2.1	0.07	308	4.4
0.20	−0.06	i_{lim}	134.6	1.7	0.10	415	3.3

* i_{lim} is the limiting current.

** The value of the current density is found by extrapolating the linear section of the anode PC for $E = -0.05$ V.

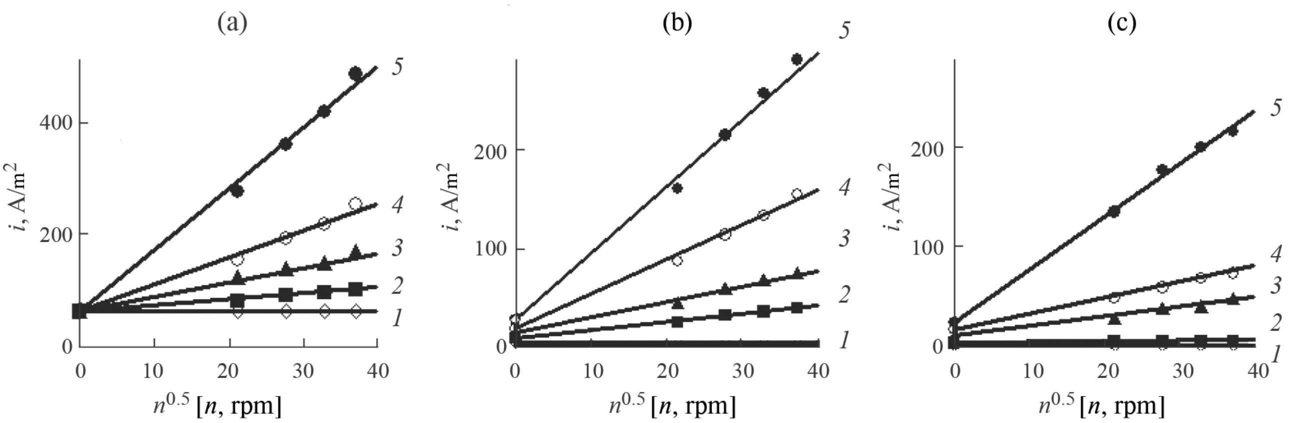

Fig. 2. Dependences of the cathodic current density on the rotation frequency of the St3 steel disk in 2 M H_2SO_4 (a), inhibited by 10 mM catamine AB (b) and 10 mM IFKhAN-92 (c), in the presence of Fe(III) (mol/l): (1) 0, (2) 0.02, (3) 0.05, (4) 0.10, (5) 0.20, $E = -0.30$ V, $t = 25°C$.

Table 2. Values of the constants i_k and f in the equation $i_c = i_k + f n^{1/2}$ for $E = -0.30$ V and effective diffusion coefficients of Fe(III) cations for the cathodic reaction of a steel rotating disk electrode in 2 M H_2SO_4 containing $Fe_2(SO_4)_3$, i_k is given in A/m^2, f is given in Amin$^{1/2}$/(m^{2}rpm.$^{1/2}$), D is given in μm^2/s, and $t = 25°C$

$C_{Fe(III)}$, M	No additives			10 mM catamine AB			10 mM IFKhAN-92		
	i_k	f	$D \times 10^{-3}$	i_k	f	$D \times 10^{-3}$	i_k	f	$D \times 10^{-3}$
0	61.5	0	–	3.8	0	–	0.4	0	–
0.02	61.5	1.0	0.14 ± 0.02	7.7	0.8	0.08 ± 0.01	2.2	0.1	0.004
0.05	61.5	2.6		13.8	1.6		9.2	1.0	0.03
0.10	61.5	4.8		16.9	3.5		15.4	1.6	0.03
0.20	61.5	11.0		26.9	6.8		23.1	5.3	0.05

disk electrode [17, 18]. In the case of laminar motion of the liquid near the surface of the rotating metal disk, the value i_d is directly proportional to the square root of the rotation frequency of the disk electrode (n), and expression (13) takes the form

$$i_c = i_k + f n^{1/2}, \tag{12}$$

where f is the intensity coefficient of the diffusion current increment. In 2 M H_2SO_4 + $Fe_2(SO_4)_3$, the experimental dependence of i_c on $n^{1/2}$ is linear (Fig. 2, Table 2). In 2 M H_2SO_4, there is no response of the cathodic current to the change in the rotation frequency of the steel disk, which indicates the kinetic nature of reaction (2). In H_2SO_4 solutions containing $Fe_2(SO_4)_3$, the kinetic component of the cathodic current of the steel electrode is the same as in the solution without $Fe_2(SO_4)_3$, indicating independence of reactions (2) and (4). Hence, reaction (2) is realized in the kinetic region while reaction (4) is realized in the diffusion region.

The diffusion current determined by reduction of Fe(III) on a steel electrode under laminar fluid flow is described by the Levich equation [16]

$$i_d = 0.62zFC^* D^{2/3} h^{-1/6} \omega^{1/2}, \tag{13}$$

where z is the number of electrons participating in the reaction taking place on the electrode, C^* is the concentration of Fe(III) in the depth of the solution, D is the diffusion coefficient of the electroactive particle, η is the kinematic viscosity of the liquid (0.011 cm^2/s [19]), and ω is the angular velocity of disk rotation. Using Eq. (15), we calculated the values $D_{Fe(III)}$ in 2 M H_2SO_4 using the values of diffusion current densities (Table 2).

In background solutions of H_2SO_4 containing $Fe_2(SO_4)_3$, reactions (2) and (4) proceed independently on steel. In further discussion of the results related to the inhibition of steel corrosion in such environments, we will proceed from the assumption that both of these partial cathodic processes are also realized independently [5].

Table 3. Values of kinetic (i_k) and diffusive (i_d) partial cathodic currents and inhibition coefficients by inhibitors of these partial cathodic currents (γ_k and γ_d) for a steel disk electrode St3 (460 rpm) in 2 M H_2SO_4, $E = -0.30$ V, i is given in A/m^2

$C_{Fe(III)}$, M	No additives		10 mM catamine AB				10 mM IFKhAN-92			
	i_k	i_d	i_k	γ_k	i_d	γ_d	i_k	γ_k	i_d	γ_d
0	61.5	0	3.8	16	0	–	0.4	150	0	–
0.02	61.5	18.5	7.7	8.0	15.4	1.2	2.2	28	1.7	11
0.05	61.5	61.6	13.8	4.5	30.8	2.0	9.2	6.7	18.5	3.3
0.10	61.5	92.3	16.9	3.6	69.3	1.3	15.4	4.0	32.3	2.9
0.20	61.5	215	26.9	2.3	135	1.6	23.1	2.7	112	1.9

The addition of 10 mM catamine AB and, especially, 10 mM IFKhAN-92 to 2 M H_2SO_4 significantly affects the parameters of electrode reactions of St3 steel (Fig. 1, Table 1). In the presence of these CI, there is an inhibition of both electrode reactions of steel St3, and E_{cor} values are shifted to the region of positive potentials as compare to the background medium by 0.11 and 0.15 V, respectively, which indicates that these substances preferentially slow down the anodic reaction of the metal. In media containing CI, the slope of cathodic polarization, as compared to the background 2 M H_2SO_4, is increased to the current limit. In such environments, there is no response of the cathodic current to the rotation frequency of the steel disk electrode (Fig. 2, Table 2), and the cathodic process, as in 2 M H_2SO_4 in the absence of $Fe_2(SO_4)_3$, is predominantly driven by reaction (2) realized with kinetic control. In the inhibited media, especially in the presence of IFKhAN-92, the values i_k are lower than in the background medium.

The presence of $Fe_2(SO_4)_3$ in the corrosive environment worsens the inhibition of CI cathodic and anodic reactions of steel, and this effect increases as the Fe(III) content in the solution grows (Fig. 1, Table 1). The response of the cathodic current to the rotation frequency of the disk electrode is observed (Fig. 2, Table 2). In such a system, the cathodic current will be the sum of the kinetic current determined by partial reaction (2) and the diffusion current determined by partial reaction (4). Increasing the content of $Fe_2(SO_4)_3$ in the inhibited acid leads to an increase in both i_k and i_d. It turns out that in the inhibited acid, Fe(III) salts accelerate the cathodic reaction, participating in it not only as an additional depolarizer, but also reduce the inhibition of CI cathodic hydrogen release, which in general negatively affects the protection of steel. It is important to note that, other conditions being equal, in the presence of IFKhAN-92 additive, the negative influence of $Fe_2(SO_4)_3$ on the inhibition of electrode reactions of steel is manifested to a much lesser extent than in the media inhibited by catamine AB.

We quantitatively evaluate the influence of the considered CI on the kinetic and diffusion components of the cathodic process on steel. For this purpose, we calculate the values of i_k and i_d of steel in 2 M H_2SO_4 at an electrode rotation speed of 460 rpm (Table 3). As the Fe(III) content in the solution grows, the proportion of cathodic reaction due to its reduction increases. In the uninhibited solution containing 0.02 M Fe(III), it is 21% while it is 78% in the presence of 0.20 M Fe(III). A similar pattern is observed in inhibited solutions. In an acid containing 0.02 and 0.2 M Fe(III) in the presence of catamine AB, the reduction fraction of Fe(III) cations is 67 and 83%, and in solution containing IFKhAN-92 it is 44 and 83%, respectively. The values of the degrees of inhibition of partial cathodic currents of steel by inhibitors show that, other conditions being equal, catamine AB and IFKhAN-92 preferentially inhibit the cathodic release of hydrogen. Increasing the concentration of Fe(III) cations simultaneously decreases the inhibition of proton and Fe(III) cation reduction by the studied CI; however, this effect in the environments containing IFKhAN-92 is weaker than in solutions with the addition of catamine AB.

One should have an idea of how the presence of CI in the aggressive environment would affect the value $D_{Fe(III)}$. The values $D_{Fe(III)}$ observed in inhibited 2 M H_2SO_4, especially in the presence of IFKhAN-92, are lower than the values characteristic of the background medium with the same parameters (Table 2). In the presence of 10 mM catamine AB, $D_{Fe(III)}$ values are approximately 40% lower than the values observed in environments without CI and do not depend on the concentration of $Fe_2(SO_4)_3$ in the solution. In contrast, when 10 mM IFKhAN-92 is added, $D_{Fe(III)}$ values are significantly lower than those observed in media without CI. The value $D_{Fe(III)}$ grows as the $C_{Fe(III)}$ content in the solution grows. We should clarify that unlike 2 M H_2SO_4 containing $Fe_2(SO_4)_3$, in inhibited media, Eq. (15) allows us to calculate the effective values of $D_{Fe(III)}$ rather than the true values. The introduction of insignificant CI additives (10 mM) into the acid solution cannot change the true value of $D_{Fe(III)}$ in it that significantly. We see another reason for this phenomenon — the inhibitor molecules adsorbing on the steel surface form polymolecular protective layers. In particular, the composition and structure of polymolecular protective layers formed by the inhibitor IFKhAN-92 are discussed in [9]. For reduction, the Fe(III) cation must overcome the protective layer to reach the steel surface. The rate of such a process will be determined by the diffusion of Fe(III) cation in the protective layer formed by the corrosion inhibitor. It is the values $D_{Fe(III)}$ in the near-surface protective layer of the inhibitor that largely determine the values of effective $D_{Fe(III)}$ obtained from Eq. (15). Note that catamine AB and IFKhAN-92 will form protective layers with different permeability with respect to Fe(III) cations on the steel surface. Probably, the surface protective layer formed by catamine AB is more permeable to Fe(III) cations as compared to the layer formed by IFKhAN-92, which is reflected in the values of effective $D_{Fe(III)}$. The high permeability of the protective layer formed by catamine AB is determined by the fact that CI molecules are bound to the metal surface by a weak physical interaction. On the contrary, IFKhAN-92 molecules, when forming a protective layer on steel in the H_2SO_4 solution, bind with the metal surface chemically, which determines a high protective effect [9].

Revealing of kinetic parameters of the studied systems allows us to predict the character of corrosion of low-carbon steel in them. Corrosion of steel in 2 M H_2SO_4 containing $Fe_2(SO_4)_3$ proceeds through stages characterized both by kinetic control and diffusion limitations. Therefore, the nature of steel corrosion in such systems should depend significantly on the nature of convection of the corrosive environment. At the same time, one should not expect effective protection of low-carbon steel in 2 M H_2SO_4 containing $Fe_2(SO_4)_3$ by adding catamine AB since this inhibitor poorly slows down partial electrode reactions of steel and, first of all, the reduction of Fe(III) cations. More promising with respect to the protection of low-carbon steel in the flow of 2 M H_2SO_4 containing $Fe_2(SO_4)_3$ is the inhibitor IFKhAN-92, which has a stronger effect on partial reactions of steel as evidenced by the data of electrochemical studies.

The assumptions we made above were confirmed when studying the corrosion of low-carbon steel in 2 M H_2SO_4 containing $Fe_2(SO_4)_3$ by mass loss of metal samples (Fig. 3, Table 4). Both in the absence of CI and in their presence, the corrosion of low-carbon steel in 2 M H_2SO_4 containing $Fe_2(SO_4)_3$ increases as $C_{Fe(III)}$ grows. Almost in all studied media, a response of the corrosion process to the rate of mixing of the corrosion medium is observed. The experimental dependence of the corrosion rate of low-carbon steel on the rotational speed of the propeller stirrer used to create forced convection of the corrosive environment can be described by the equation

$$k = k_{st} + \lambda w^{1/2}, \tag{14}$$

where k_{st} is the corrosion of low-carbon steel in the static medium, w is the rotation frequency of propeller stirrer, λ is the empirical coefficient characterizing the intensity of corrosion rate increments. Equation (16) formally corresponds to Eq. (14) characterizing electrode reactions proceeding with diffusion control. When discussing the obtained experimental dependences, one should take into account that, according to the laws of diffusion kinetics, only the kinetic component of the corrosion process can be realized in a static medium, and the diffusion component, due to the absence of fluid motion, will not be realized. Then, the values k_{st} obtained in media containing $Fe_2(SO_4)_3$ should equal the value k_{st} in 2 M H_2SO_4, where the process is realized exclusively in the kinetic mode. The actual values k_{st} observed in media containing $Fe_2(SO_4)_3$ are significantly higher than in 2 M H_2SO_4. This effect is the result of natural convection occurring in a static corrosive environment. It is further enhanced by the abundant release of hydrogen gas during the corrosion process on a sufficiently large surface area of the steel samples. Forming and popping hydrogen bubbles can strongly mix the corrosive medium. In the transition from static corrosion medium to dynamic corrosion medium, this effect is leveled out as the propeller stirrer speed increases. Note that in 2 M H_2SO_4, both in the absence of CI and in their presence, an insignificant response of the corrosion process to an increase in the flow rate of the corrosive medium is observed, which is explained by the presence of dissolved air oxygen in the considered media. Since the observed effect of oxygen is insignificant, we will not take it into account in our further discussions.

The analysis of experimental data shows that an increase in the content of $Fe_2(SO_4)_3$ in the corrosion medium accelerates the corrosion of low-carbon steel (Table 5). The most significant increase in $C_{Fe(III)}$ affects the corrosion rate of steel in the medium containing no inhibitors. Also, in the presence of $Fe_2(SO_4)_3$ in the H_2SO_4 solution, the corrosion of steel accelerates in the transition from static to dynamic medium. For instance, at $C_{Fe(III)} = 0.1$ M in 2 M H_2SO_4,

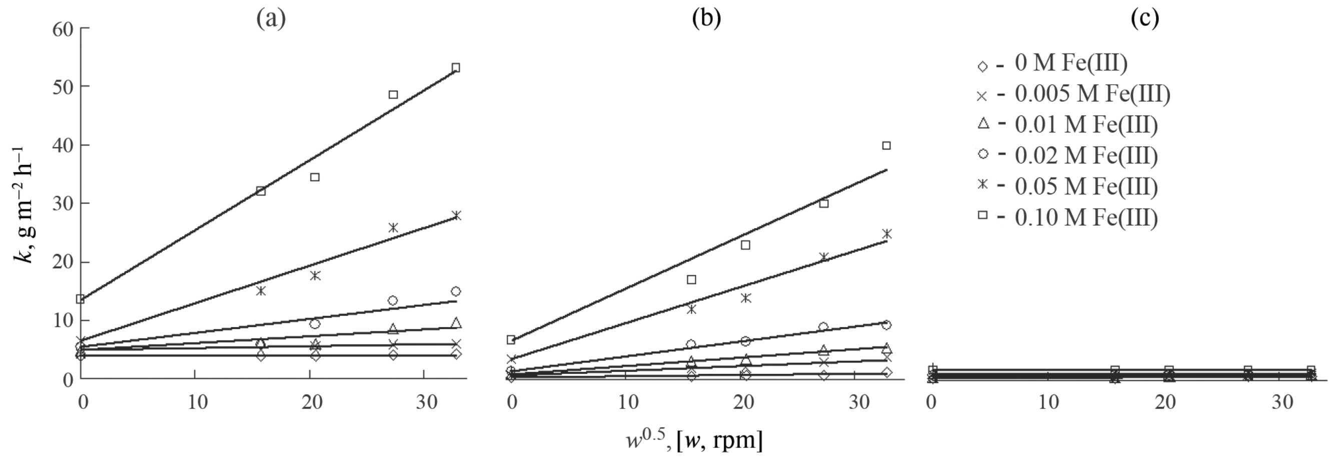

Fig. 3. Dependences of the corrosion rate of steel St3 in 2 M H_2SO_4 containing Fe(III) on the propeller stirrer rotation speed in the corrosive medium, (a) with no inhibitor, (b) 10 mM catamine AB, and (c) 10 mM IFKhAN-92. Duration of experiments is 2 h, $t = 20 \pm 2°C$.

Table 4. Values of the constants k_{st} and λ in the equation $k = k_{st} + \lambda w^{1/2}$ for corrosion of low-carbon steel 08ps in 2 M H_2SO_4 containing $Fe_2(SO_4)_3$, k_{st} is given in $g/(m^2h)$, λ is given in $gh^{1/2}/(m^2rpm^{1/2})$. Duration of experiments is 2 h, $t = 20 \pm 2°C$.

$C_{Fe(III)}$, M	No additives		10 mM catamine AB		10 mM IFKhAN-92	
	k_{st}	λ	k_{st}	λ	k_{st}	λ
0	4.0	0.005	0.43	0.019	0.35	0.013
0.005	4.2	0.060	0.77	0.081	0.38	0.014
0.01	4.8	0.125	0.90	0.142	0.58	0.011
0.02	5.5	0.152	1.5	0.253	0.84	0.004
0.05	6.4	0.644	3.5	0.614	1.0	0.004
0.10	13.6	1.189	6.7	0.892	1.8	0

not containing inhibitor, transition from the static medium to the dynamic one ($w = 780$ rpm) is accompanied by an increment of corrosion losses $\Delta k = 35$ $g/(m^2h)$. At the same time, the corrosion rate of steel in the static medium is $k_{st} = 14$ $g/(m^2h)$, which is significantly lower.

In 2 M H_2SO_4, in the absence of $Fe_2(SO_4)_3$, additives of organic CI significantly inhibit the corrosion of 08ps steel. The maximum protective effect is shown by IFKhAN-92 for which the values of k_{st} and λ are maximally reduced as compared to the background medium (Table 5). In the background solution H_2SO_4, as well as in the medium containing catamine AB, the presence of Fe(III) salts increases the values of parameters k_{st} and λ The higher the $C_{Fe(III)}$, the stronger is the negative influence of $Fe_2(SO_4)_3$ on the corrosion of steel in the flow of the aggressive medium. In 2 M H_2SO_4 inhibited by IFKhAN-92, the effect of $Fe_2(SO_4)_3$ addition is somewhat different. Increasing the Fe(III) content in the corrosive medium increases the value of the parameter k_{st}, but generally decreases the value of the parameter λ. As a result, $k \leqslant 1.8$ $g/(m^2h)$ is maintained under all experimental conditions, including media flow tests.

The high efficiency of 10 mM IFKhAN-92 in inhibition of corrosion of 08ps steel in the flow of the H_2SO_4 solution containing Fe2(SO4)3 as compared to the background medium or medium containing 10 mM catamine AB is clearly demonstrated by the data on the incremental corrosion losses of steel in these media as a result of transition from static to dynamic conditions or as the content of $Fe_2(SO_4)_3$ in the corrosion medium grows (Table 5).

Comparison of the inhibitory action of 10 mM catamine AB and 10 mM IFKhAN-92 in protecting 08ps steel in 2 M H_2SO_4 containing $Fe_2(SO_4)_3$ shows

Table 5. Corrosion rate (k), corrosion loss increment (Δk), and corrosion acceleration factor (γ^{-1}) of 08ps steel in 2 M H_2SO_4 containing $Fe_2(SO_4)_3$, k and Δk are given in g/(m^2h). Duration of experiments is 2 h, $t = 20 \pm 2$°C

$C_{Fe(III)}$, M	Static medium			Dynamic medium (780 rpm)			Δk_{dyn}**	γ_{dyn}^{-1**}
	k	$\Delta k_{Fe(III)}$*	$\gamma_{Fe(III)}^{-1*}$	k	$\Delta k_{Fe(III)}$	$\gamma_{Fe(III)}^{-1}$		
No inhibitor								
0	4.0	0	1.0	4.1	0	1.0	0.10	1.0
0.005	4.2	0.2	1.1	5.9	1.8	1.4	1.7	1.4
0.01	4.8	0.8	1.2	8.5	4.4	2.1	3.7	1.8
0.02	5.5	1.5	1.4	11	6.6	2.7	5.5	2.0
0.05	6.4	2.4	1.6	26	22	6.3	20	4.1
0.10	14	10	3.5	49	45	12	35	3.5
10 mM catamine AB								
0	0.43	0	1.0	0.77	0	1.0	0.34	1.8
0.005	0.77	0.34	1.8	2.9	2.1	3.7	2.1	3.8
0.01	0.90	0.47	2.1	5.2	4.4	6.8	4.3	5.7
0.02	1.5	1.1	3.5	9.0	8.2	12	7.5	6.0
0.05	3.5	3.1	8.1	21	20	27	18	6.0
0.10	6.7	6.3	16	30	29	39	23	4.5
10 mM IFKhAN-92								
0	0.35	0	1.0	0.77	0	1.0	0.42	2.2
0.005	0.38	0.03	1.1	0.80	0.03	1.0	0.42	2.1
0.01	0.58	0.20	1.5	0.92	0.15	1.2	0.34	1.6
0.02	0.84	0.49	2.4	0.95	0.18	1.2	0.11	1.1
0.05	1.0	0.64	2.9	1.1	0.33	1.4	0.10	1.1
0.10	1.8	1.5	5.1	1.8	1.0	2.3	0	1.0

* Change in value due to the presence of Fe(III) in the solution given the same solution flow rate.

** Change in value due to the acceleration of the solution flow given the constant Fe(III) content in it.

higher protective effects of the substituted triazole in both static and dynamic environments (Table 6). Increasing Fe(III) content significantly decreases the protective effects of catamine AB in static and dynamic environments. For IFKhAN-92, there is an insignificant decrease in the protective effect in static conditions of corrosion tests. In contrast, an increase in the protective effect is observed in the dynamic environment.

Differences in the protective efficiency of catamine AB and IFKhAN-92 are due to differences in the nature of their adsorption interaction with the metal. The reason for the decrease in protective effect of catamine AB in the presence of $Fe_2(SO_4)_3$ is the acceleration of the cathodic reaction of steel, shifting its E_{cor} to the region of higher potentials at which the metal surface has a positive charge, which, as shown in the work of Antropov [20], worsens the physical adsorption of organic cations on it. IFKhAN-92 molecules are bound to the metal surface by chemical interaction.

Interestingly, the differences in the effectiveness of IFKhAN-92 and catamine AB obtained during corrosion tests are significantly higher than predicted from the data of electrochemical studies. The reasons for these differences lie in the fact that during electrochemical studies, the metal is constantly under severe conditions of forced polarization, when electrode reactions on the metal proceed at rates much higher than those realized for E_{cor}. Apparently, forced polarization of the electrode imposes undesirable effects on the IFKhAN-92 protective properties.

We obtained a result of important theoretical and practical significance. We showed that if we use substances capable of chemisorbing on the metal surface as corrosion retarders, we can ensure effective protection of steels in the flow of acid solution

Table 6. Corrosion inhibition coefficients (γ) of 08ps steel in 2 M H_2SO_4 containing $Fe_2(SO_4)_3$ by the corrosion inhibitors involved. Duration of experiments is 2 h, $t = 20 \pm 2$°C

$C_{Fe(III)}$, M	10 mM catamine AB		10 mM IFKhAN-92	
	Static medium	Dynamic medium (780 rpm)	Static medium	Dynamic medium (780 rpm)
0	9.3	5.3	11	5.3
0.005	5.5	2.0	11	7.4
0.01	5.3	1.6	8.3	9.2
0.02	3.7	1.2	6.5	12
0.05	1.8	1.2	6.4	24
0.10	2.1	1.6	7.8	27

containing Fe(III) salts. For the first time, an individual inhibitor — IFKhAN-92, capable of protecting steel in the flow of H_2SO_4 solution containing $Fe_2(SO_4)_3$, was proposed. Under the most severe conditions of the flow of aggressive medium containing 0.1 M Fe(III), the addition of 10 mM IFKhAN-92 slows down the corrosion of low-carbon steel almost 30 times, yielding $k = 1.8$ g/(m^{2}h).

CONCLUSIONS

(1) Corrosion of low-carbon steel in a dynamic solution of H_2SO_4 containing $Fe_2(SO_4)_3$ accelerates as the flow rate of the medium and concentration of Fe(III) salt in it grow. The empirical dependence of the steel corrosion rate on the flow rate of the studied media stirred by a propeller stirrer can be represented as a linear dependence

$$k = k_{st} + \lambda w^{1/2},.$$

where k_{st} is the corrosion rate of steel in the static medium, w is the rotation frequency of the propeller stirrer, and λ is the empirical coefficient.

(2) Corrosion of low-carbon steel in the flow of H_2SO_4 solution containing $Fe_2(SO_4)_3$ is realized as a result of three partial reactions on the metal, viz. anodic ionization of iron and cathodic reduction of Fe(III) protons and cations.

(3) We studied the possibility of inhibitor protection of low-carbon steel in the flow of H_2SO_4 solution containing $Fe_2(SO_4)_3$ by additives of IFKhAN-92 and catamine AB. We showed the inhibitor IFKhAN-92, unlike catamine AB, to significantly slow down steel corrosion in these media. The reason of higher inhibitor effects of IFKhAN-92 when it comes to protection of steel in the media involved, as compared to catamine AB, lies in its more effective retardation of partial electrode reactions of metal, viz. anodic ionization of iron and cathodic reduction of Fe(III) protons and cations.

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