Cathodic reduction of hydrogen on low-carbon steel in solutions of mineral acids containing nitrogen-containing organic compounds

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Abstract

The effect of corrosion inhibitors, namely a quaternary ammonium salt (Catamine AB) and 3-substituted 1,2,4-triazole (IFKhAN-92), on the corrosion and hydrogen charging of 08kp low-carbon steel and 70S2KhA high-strength steel in H₂SO₄ and HCl solutions has been studied. Both inhibitors efficiently inhibit the corrosion and hydrogen charging of these steels. It was found that the addition of Catamine AB and IFKhAN-92 significantly inhibits the hydrogen evolution in H₂SO₄ and HCl solutions on cathodically polarized low-carbon steel 08kp. These compounds slow down both partial reactions of this process on steel, *i.e.*, hydrogen molization and its incorporation into the metal bulk, in a wide range of cathodic potentials. IFKhAN-92 provides the strongest inhibition of these partial reactions. Partial or total prevention of the hydrogen charging of steels by addition of nitrogen-containing compounds during corrosion in H₂SO₄ and HCl solutions is largely due to a decrease in the rate of hydrogen penetration into the metals by these compounds. Analysis of experimental data on the protection of steels in acid solutions with nitrogen-containing compounds allowed us to conclude that industrial application of IFKhAN-92 as a corrosion inhibitor of steels in these very corrosive environments is a promising approach. It is important that this corrosion inhibitor slows down the corrosion and hydrogen charging of various steels in H₂SO₄ and HCl solutions that are industrially significant acid environments.

Keywords: *acid corrosion, corrosion inhibitors, triazole, low carbon steel, high strength steel, hydrogen charging of steel, hydrogen permeation, sulfuric acid, hydrochloric acid.*

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Introduction

The operation of steel structures in contact with very corrosive aqueous media often not only results in corrosion damage but is also accompanied by hydrogen charging of a metal that can significantly impair its mechanical characteristics [1–3]. In this respect, acid solutions where hydrogen is one of the main products of steel corrosion are extremely dangerous.

Hydrogen is released on the metal surface in gaseous form and partially penetrates into the metal bulk [4, 5].

The use of corrosion inhibitors (CIs) is an efficient method for steel protection in these environments. Nitrogen-containing organic compounds slow down the corrosion of various steels in solutions of HCl [6–16], H₂SO₄ [6, 7, 17–21], H₃PO₄ [22–24], and HNO₃ [25]. Among such CIs, quaternary ammonium salts (QAS) deserve attention because many of them can slow down the corrosion of steels significantly [26–36]. Recently, organic compounds containing two or more quaternized nitrogen atoms in their structure have been studied extensively [37–43]. The protective effect of QAS can be enhanced by combining them with some anionic and molecular additives [44–47], which makes them promising as a basis for creating mixed CIs. Triazole derivatives that have been extensively studied in recent decades [48–63] may become an alternative to QAS as CIs for steels in acid media. The efficient inhibition of steel corrosion in acids by compounds of these groups results from a considerable slowdown of electrode reactions on the metal by these additives. Despite the large number of studies dealing with the effect of nitrogen-containing organic CIs on the corrosion of steels in acid media, their effect on the penetration of cathodically evolved hydrogen into a metal is usually not considered. It was shown previously [64–69] that, along with the inhibition of the cathodic reaction, the addition of nitrogen-containing compounds slows down the rate of hydrogen penetration into a metal.

The practical significance of QAS and triazole derivatives as CIs of steels in acid media largely determines the importance of comparative determination of the effect of compounds of these classes on the penetration of cathodically evolved hydrogen into steel. Moreover, it is of interest to identify the possible relationship between the hydrogen charging of steels in an inhibited corrosive medium in the course of corrosion and the penetration rate of evolved hydrogen into steel.

Experimental

Aqueous 2 M solutions of H₂SO₄ and HCl were used as the backgrounds. All the solutions were prepared from reagent grade chemicals and distilled water. Solutions deaerated with argon were used in electrochemical studies. Corrosion tests were carried out in solutions with free access of air. Catamine AB, which is a mixture of alkylbenzyltrimethylammonium chlorides ($[C_nH_{2n+1}N^+(CH_3)_3CH_2C_6H_5]Cl^-$, where $n=10-18$), was used as the QAS. The IFKhAN-92 inhibitor (a derivative of 3-substituted 1,2,4-triazole) was also studied. Due to the low solubility of IFKhAN-92, it was added to the acid solutions as a concentrated solution in ethanol, such that the concentration of ethanol in the etching solutions was 0.24 mol/L. The experiments were carried out using samples of 08kp low-carbon steel and 70S2KhA steel. The steel compositions are given in Table 1.

Table 1. Chemical composition of 08kp and 70S2KhA steels (mass%).

Steel grade	Elements								
	C	Si	Mn	Ni	S	P	Cr	Cu	Al
08kp	0.05	0.03	0.38	0.09	0.04	0.035	0.05	0.15	0.16
70S2KhA	0.7	1.52	0.52	–	–	–	0.3	–	–

Devanatkhan–Stakhursky electrochemical method

It is generally accepted [70, 71] that the cathodic hydrogen evolution process in acids occurs through the stage of discharge of H^+ ions:

followed by removal of adsorbed hydrogen atoms from the metal surface by electrochemical desorption:

and/or chemical recombination:

In parallel to desorption stages (2) and (3), exchange of hydrogen atoms between the surface and the metal phase occurs:

It is assumed that the cathodic evolution of hydrogen on iron occurs by the “discharge–chemical recombination, double rate control” [72] or “slow discharge–irreversible chemical recombination” mechanisms [73]. It is believed that the discharge of H^+ ions occurs on the metal surface not occupied with adsorbed atomic hydrogen.

The rate of electrochemical desorption or chemical recombination under steady-state conditions can be calculated as:

$$i_{mol} = i_c - i_{dif} \quad (5)$$

where i_c is the cathodic current density; i_{dif} is the penetration current density.

The kinetics of cathodic evolution and incorporation of hydrogen into steel was studied by the electrochemical hydrogen desorption method [74, 75]. The essence of the method is that one (working) side of a metal membrane is polarized cathodically. Anodic potential is applied to the other (diffusion) side, so complete ionization of hydrogen atoms diffusing through the membrane occurs in the alkali solution at that potential. The current consumed for the ionization of hydrogen that diffuses through the membrane is measured. It allows one to judge both on the amount and rate of hydrogen diffusion. In the case of an iron or steel

membrane, this side is coated with a thin palladium layer in order to enhance the oxidation of hydrogen and reduce the corrosive current on the output side.

The measurements were carried out in a Devanatkhan–Stakhursky electrochemical cell with a vertical membrane (Figure 1). A constant potential ($E=\text{const}$) was applied to the working side of the membrane and the external current (i_s) was measured. The steady-state current of hydrogen penetration through the membrane (i_{dif}) was recorded on the anodically polarized (diffusion) side of the membrane. The potential of the working membrane side was shifted from 0.4 V in the positive direction at 0.02 V steps. The exposure time at each potential was 30 minutes. The working part of the cell was filled with acid solutions containing various CIs. The diffusion part of the cell was filled with 0.1 N NaOH and the membrane was polarized at $E=0.65$ V, which provided hydrogen ionization under conditions of limiting diffusion flux of hydrogen atoms in the membrane. The background current in the experiments did not exceed $1 \cdot 10^{-2}$ A/m². Polarization was provided by a PI-50 potentiostat with a PR-8 programmer.

Figure 1. Devanatkhan–Stakhursky electrochemical cell. 1 – working electrode (membrane); 2 – Teflon holder; 3 – working part of the cell; 3' – diffusion part of the cell; 4, 4' – auxiliary electrode cell; 5, 5' – auxiliary electrode; 6, 6' – electrolytic switch; 7, 7' – reference electrode; 8, 8' – tap for draining the solution; 9, 9' – solution input into the cell; 10 – argon input into the cell; 11 – water seal.

To simplify hydrogen ionization, a membrane made of 08kp steel (0.1 mm thick) was covered with a palladium layer on the diffusion side. Before palladium plating, the electrode surface was degreased with acetone, chemically etched for 15 minutes in 15% HCl solution, washed with distilled water, and dried with filter paper. After that, one side was coated with

a varnish. The palladium plating solution had the composition (per liter): PdCl_2 –25 g, NH_4OH –20 g, maleic anhydride in the amount required to set $\text{pH}=8.5$ – 9.5 .

Palladium plating mode: $I=100$ mA ($23.5 \cdot 10^{-3}$ A/cm²), $\tau=100$ s as described in [76]. The thickness of the resulting coating was $2.7 \cdot 10^{-7}$ m. The working area of the membrane was 25–40% of the total area, which made it possible to prevent the possible edge effect on hydrogen penetration. The membrane was kept for at least 2 days before use.

Immediately before the experiment, the palladium-free side of the electrode surface was cleaned with a “0” emery paper. Then the electrode was degreased with acetone, washed with distilled water, dried with filter paper, and placed in a cell.

To fill the hydrogen traps existing both in the metal bulk and on its surface, it was kept at $E=-0.4$ V ($\tau=60$ min) on the working side of the diaphragm until a reproducible penetration current was established [77].

Gravimetric method

The corrosion rate of steel was determined by the gravimetric method after 2 h of exposing the samples to 2 M H_2SO_4 and 2 M HCl solutions. Electrodes of two steel grades were used: 08kp, 0.5 mm thick with a working surface area of $S=20$ cm², and 70S2KhA, 0.5 mm thick with a working surface area of $S=17.6$ cm². The mass loss of samples (at least 3 samples per point) was determined using 50 ml of an acid solution per sample.

Before an experiment, samples of 08kp steel were cleaned on an abrasive wheel (ISO 9001, grit 60) and degreased with acetone. The factory preservative formulation was removed with hexane from 70S2KhA steel samples. Their surfaces were activated for 1 min with a mixture of acetone and concentrated HCl (10:1) and wiped dry with a cotton cloth.

Vacuum extraction method

The hydrogen charging of 70S2KhA and 08kp steels was determined by vacuum extraction. After a corrosion test, a sample was placed into a vessel that was then evacuated to a residual pressure of $1.33 \cdot 10^{-4}$ Pa and heated to a temperature of $t=500^\circ\text{C}$. The amount of hydrogen released upon heating a sample in vacuum was estimated from the pressure change in 10 min (P_{total}) measured with a McLeod gauge at a constant volume of the vacuumized part of the system. The pressure of evolved hydrogen (P_{H_2}) was calculated from the change in the total pressure (P_{total}) by the formula:

$$P_{\text{H}_2} = P_{\text{total}} - P_{\text{correct}} \quad (6)$$

where P_{correct} is the correction for the blank test.

The volume concentration of hydrogen in a steel (cm³/100 g steel) was calculated by the formula:

$$V_{\text{H}_2} = \frac{100KP_{\text{H}_2}}{M} \quad (7)$$

where K is a constant associated with the volume of the analytical part of the setup; M is the mass of the steel sample, grams.

Data on the hydrogen charging of metals were reported after adjustment for the metallurgical hydrogen that amounts to $0.34 \text{ cm}^3/100 \text{ g}$ for 70S2KhA steel and $0.57 \text{ cm}^3/100 \text{ g}$ for 08kp steel.

The effect of a CI on the rate of the cathodic process on steel in acid solutions was estimated using the inhibition coefficient

$$\gamma = \frac{i_0}{i_{\text{in}}} \quad (8)$$

where i_0 and i_{in} are current densities in the background solution and in the solution with an additive under study.

The efficiency of steel corrosion inhibition was estimated by the degree of protection

$$Z = \left[\frac{k_0 - k_{\text{in}}}{k_0} \right] \cdot 100\% \quad (9)$$

where k_0 and k_{in} are corrosion rates in the background solution and in the solution with a CI.

The degree of steel protection from hydrogen charging was determined by the formula:

$$Z_{\text{H}_2} = [(V_{\text{H}_2}^0 - V_{\text{H}_2}^{\text{in}}) / V_{\text{H}_2}^0] \cdot 100\% \quad (10)$$

where $V_{\text{H}_2}^0$ and $V_{\text{H}_2}^{\text{in}}$ represent the hydrogen charging of steel in the background solution and in the inhibited solution.

The electrode potentials are reported *versus* the standard hydrogen electrode.

Results and Discussion

Cathodic reduction of hydrogen on low-carbon steel in solutions of mineral acids

Cathodic polarization curves on 08kp steel and the plots of the rate of hydrogen penetration into the metal *versus* the potential were obtained both in background acid solutions and in solutions containing a CI (Figures 2–5). The experimental values of cathodic current density and hydrogen penetration current were used to calculate the rates of molization in solutions with various compositions. As one can see, the slope of the cathodic polarization curve on steel in 2 M H_2SO_4 solution is $b_c = 0.120 \text{ V}$ (Figure 2, Table 2), which is typical of steel in this environment [78]. In the H_2SO_4 solution, the evolved hydrogen is mainly converted to the molecular form while only a small fraction penetrates into the metal. For example, at $E = -0.300 \text{ V}$, the fraction of hydrogen incorporated into the metal is 17%.

Figure 2. Plots of cathodic current density (a), penetration current (b), and hydrogen molization current (c) vs. the potential of the steel membrane in 2 M H₂SO₄ containing Catamine AB. $t=25^{\circ}\text{C}$.

Figure 3. Plots of cathodic current density (a), penetration current (b), and hydrogen molization current (c) vs. the potential of the steel membrane in 2 M H₂SO₄ containing IFKhAN-92. $t=25^{\circ}\text{C}$.

The addition of Catamine AB to 2 M H₂SO₄ significantly slows down the rate of hydrogen evolution on steel. In the entire concentration range studied, addition of the CI to

the sulfuric acid solution does not change the slope of the cathodic polarization curve. At $C_{\text{Catamine AB}}=0.01\text{--}10\text{ mM}$, the cathodic current density of steel at $E=-0.300\text{ V}$ decreases 2.5–6.5 fold. Both partial processes that consume the generated hydrogen, *i.e.*, its molization and diffusion into steel, are inhibited. The former process slows down 2.6–7.7 fold, while the latter, 2.0–3.7 fold. In the presence of Catamine AB, the fraction of hydrogen incorporated into the metal increases and amounts to 30% at its maximum concentration of $C=10\text{ mM}$.

Table 2. Slope of the cathodic polarization curve (b_c), cathodic current density (i_c), penetration current (i_{dif}), hydrogen molization current (i_{mol}), coefficients of inhibition of cathodic current (γ_c), penetration current (γ_{dif}) and molization current (γ_{mol}) on a steel membrane (at $E=-0.300\text{ V}$) in $2\text{ M H}_2\text{SO}_4$. The potentials are given in V, the current density in A/m^2 $t=25^\circ\text{C}$.

C_{in}, mM	b_c	i_c	γ_c	i_{dif}	γ_{dif}	i_{dif}/i_c	i_{mol}	γ_{mol}
–	0.120	10.6	–	1.8	–	0.17	8.8	–
Catamine AB								
0.01	0.120	4.28	2.5	0.88	2.0	0.21	3.40	2.6
0.05	0.120	2.61	4.1	0.68	2.6	0.26	1.93	4.6
0.1	0.120	2.43	4.4	0.64	2.8	0.26	1.79	4.9
0.5	0.120	2.40	4.4	0.62	2.9	0.26	1.78	4.9
1.0	0.110	2.30	4.6	0.59	3.1	0.26	1.71	5.2
5.0	0.110	1.83	5.8	0.54	3.3	0.30	1.29	6.8
10	0.110	1.63	6.5	0.49	3.7	0.30	1.14	7.7
IFKhAN-92								
0.01	0.120	4.1	2.6	0.8	2.3	0.20	3.3	2.7
0.05	0.120	1.8	5.9	0.4	4.5	0.22	1.4	6.3
0.1	0.120	0.83	12.7	0.25	7.2	0.30	0.58	15.2
0.5	0.120	0.22	48.2	0.09	20.0	0.41	0.13	67.7
1.0	0.130	0.13	81.5	0.06	30.0	0.46	0.07	126
5.0	0.145	0.095	112	0.044	41.0	0.46	0.051	173
10	0.170	0.088	120	0.043	41.8	0.49	0.045	196

It has been shown that IFKhAN-92 significantly affects the rate of cathodic hydrogen evolution in $2\text{ M H}_2\text{SO}_4$ (Figure 3). In the presence of the triazole derivative, the slope of the cathodic polarization curve systematically increases with an increase in its content in the solution to reach a considerable value of 0.170 V . Such a high slope of the cathodic polarization curve on steel indirectly indicates that a polymolecular protective layer is

formed by the CI molecules on the metal surface. IFKhAN-92 inhibits the cathodic reaction more strongly than Catamine AB, namely, 2.6–120 fold. The penetration of hydrogen into the metal is reduced 2.3–41.8 fold, while its molization is reduced even more strongly, 2.7–196 fold. The addition of IFKhAN-92 more strongly increases the fraction of cathodic hydrogen incorporated into the metal than the QAS being studied: it increases to 49% at $C_{\text{IFKhAN-92}}=10$ mM. However, the rate of hydrogen penetration into steel in the presence of IFKhAN-92 is the smallest.

The cathodic reaction on steel in 2 M HCl (Figure 4, Table 3) occurs at a lower rate than in 2 M H₂SO₄, and the slope of the cathodic polarization curve is close to the values predicted by theory [78]. In this environment, the fraction of hydrogen incorporated into the metal is slightly smaller than in the H₂SO₄ solution.

Figure 4. Plots of cathodic current density (a), penetration current (b), and hydrogen molization current (c) vs. the potential of the steel membrane in 2 M HCl containing Catamine AB. $t=25^\circ\text{C}$.

In this acid chloride environment, Catamine AB reduces the rate of hydrogen evolution somewhat better than in the sulfate solution. The increase in the slope of the cathodic polarization curve observed in the presence of this additive is insignificant. Addition of 0.01–10 mM Catamine AB slows down the cathodic reaction on steel at $E=-0.300$ V by a factor of 2.6–14.3. At the same time, the QAS strongly reduces the molization of hydrogen and the rate of its penetration into steel. These processes are inhibited 2.5–15.1 and 2.7–10.0 fold, respectively. Catamine AB insignificantly increases the fraction of hydrogen incorporated into steel compared to the background solution. The maximum fraction of hydrogen incorporated into the metal is as small as 16%.

Table 3. Slope of the polarization curve (b_c), cathodic current density (i_c), penetration current (i_{dif}), hydrogen molization current (i_{mol}), coefficients of inhibition of cathodic current (γ_c), penetration current (γ_{dif}) and molization current (γ_{mol}) on a steel membrane (at $E=-0.300$ V) in 2 M HCl. The potentials are given in V, the current density in A/m^2 $t=25^\circ C$.

C_{in}, mM	b_c	i_c	γ_c	i_{dif}	γ_{dif}	i_{dif} / i_c	i_{mol}	γ_{mol}
—	0.115	7.6	—	0.8	—	0.11	6.8	—
Catamine AB								
0.01	0.100	3.0	2.6	0.3	2.7	0.10	2.7	2.5
0.05	0.110	0.89	8.5	0.14	5.7	0.16	0.75	9.1
0.1	0.120	0.67	11.3	0.11	7.3	0.16	0.56	12.1
0.5	0.125	0.66	11.5	0.10	8.0	0.15	0.56	12.1
1.0	0.125	0.65	11.7	0.10	8.0	0.15	0.55	12.4
5.0	0.125	0.57	13.3	0.09	8.9	0.16	0.48	14.2
10	0.125	0.53	14.3	0.08	10.0	0.15	0.45	15.1
IFKhAN-92								
0.01	0.115	6.9	1.1	0.6	1.3	0.09	6.3	1.1
0.05	0.115	3.3	2.3	0.3	2.7	0.09	3.0	2.3
0.1	0.115	1.7	4.5	0.2	4.0	0.11	1.5	4.5
0.5	0.115	0.45	16.9	0.10	8.0	0.22	0.35	19.4
1.0	0.115	0.18	42.2	0.05	16.0	0.28	0.13	52.3
5.0	0.150	0.110	69.1	0.030	26.7	0.27	0.080	85.0
10	0.195	0.108	69.1	0.029	27.6	0.27	0.079	86.1

In 2 M HCl, the addition of IFKhAN-92 (Figure 5) proved to be an efficient inhibitor of steel hydrogen charging. At a high content of triazole ($C \geq 5.0$ mM), the slope of the cathodic polarization curve is considerable. At $E=-0.300$ V, the cathodic current density decreases 69.1-fold. The rate of hydrogen diffusion into the metal decreases 27.6-fold, and the rate of its molization decreases 86.1-fold. It is interesting that at $C_{IFKhAN-92} < 0.1$ mM the fraction of hydrogen penetrating into the metal is smaller than in the background medium, whereas at $C_{IFKhAN-92} > 0.1$ mM it is somewhat larger. In the HCl solution in the presence of high C_{in} of the triazole, the fraction of hydrogen incorporated into the metal is higher than in the media inhibited by Catamine AB.

Figure 5. Plots of cathodic current density (a), penetration current (b), and hydrogen molization current (c) vs. the potential of the steel membrane in 2 M HCl containing IFKhAN-92. $t=25^{\circ}\text{C}$.

Table 4. Effect of nitrogen-containing inhibitors (5.0 mM) on the corrosion and hydrogenation of 08kp steel in 2 M H_2SO_4 and 2 M HCl. The etching duration was 2 h.

Acid	Inhibitor	k , g/(m ² ·h)	Z_{cor} , %	$V_{\text{H}_2}^*$, cm ³ /100 g	Z_{H_2} , %
25°C					
H_2SO_4	—	12	—	m.h.**	—
	Catamine AB	2.0	83.3	m.h.	—
	IFKhAN-92	0.22	98.2	m.h.	—
HCl	—	2.3	—	m.h.	—
	Catamine AB	0.52	77.4	m.h.	—
	IFKhAN-92	0.13	94.3	m.h.	—
60°C					
H_2SO_4	—	250	—	0.67	—
	Catamine AB	14	94.4	0.36	46.3
	IFKhAN-92	0.65	99.7	m.h.	100
HCl	—	54	—	m.h.	—
	Catamine AB	3.3	93.9	m.h.	—
	IFKhAN-92	0.69	98.7	m.h.	—

* Data were adjusted for metallurgical hydrogen amount, which is 0.57 cm³/100 g steel.

** m.h.—the hydrogen content in the samples does not exceed the amount of metallurgical hydrogen.

Thus, IFKhAN-92 inhibits the cathodic reaction on steel more strongly than Catamine AB. Both CIs not only inhibit the rate of hydrogen molization but also reduce the rate of its incorporation into the metal. It is important to note that the observed protective effects are observed in a wide range of cathodic potentials. The substituted triazole inhibits these processes most strongly. It is logical to assume that efficient inhibition of the rate of hydrogen penetration into the metal by this triazole would reduce the hydrogen charging of steel during corrosion. If Catamine AB is used as the CI of steel, a decrease in the degree of metal hydrogen charging should also occur but the observed effect should be smaller. This hypothesis can be confirmed by studying steel corrosion and hydrogenation processes in solutions of sulfuric and hydrochloric acids, both in the absence and in the presence of nitrogen-containing CIs.

Corrosion and hydrogen charging of steel in acid solutions

According to the data of 2-hour tests, the corrosion of steel 08kp in 2 M H₂SO₄ (25°C) occurs without hydrogen charging of the metal (Table 4). There is only a seeming contradiction with our earlier data here. The penetration of hydrogen into the metal is studied under forced cathodic polarization of steel, so the rate of hydrogen reduction on the metal surface is by orders of magnitude faster than at the corrosion potential (E_{cor}). As a result, the evolution of hydrogen is not as efficient at E_{cor} as under cathodic polarization and it does not have enough time to penetrate into the metal during the experiment. The CIs studied efficiently inhibit the corrosion process under these conditions. Hydrogen charging of steel does not occur in the presence of these compounds, just as it was predicted on the basis of the data of electrochemical studies discussed above. This is important from the practical point of view, since while some CIs used to protect steels in acid environments efficiently inhibit the corrosion of a metal, they can increase its hydrogen charging, which is very undesirable [4, 5]. A similar picture is observed both in uninhibited and inhibited 2 M HCl, with the only difference that the corrosion rate of 08kp steel is smaller in all the cases. It is important that IFKhAN-92 more efficiently inhibits the corrosion of steel in solutions of sulfuric and hydrochloric acids than Catamine AB.

We made the assumption that increasing the temperature (t) of a corrosive medium would clarify the effect of a CI on the hydrogen charging of 08kp steel during corrosion. An increase in t would accelerate hydrogen evolution on steel surface at E_{cor} , which should facilitate its penetration into the metal. Indeed, the steel corrosion rate (k) in 2 M H₂SO₄ at 60°C is 21 times higher than that at 25°C. As a result, absorbed hydrogen is trapped in steel. It is important that the organic compounds studied not only significantly inhibit the corrosion of steel under these extremely drastic conditions but also prevent its hydrogen charging. At the same time, in contrast to Catamine AB, IFKhAN-92 totally prevents the hydrogen charging of steel. In 2 M HCl (60°C), where the values of k both in the background medium and in the presence of a CI are lower than in 2 M H₂SO₄, hydrogen charging of steel does not occur in any of the cases. In this environment, Catamine AB and especially IFKhAN-92 greatly slow down the corrosion of steel.

Since low-carbon steel 08kp shows resistance to hydrogen charging under the conditions of corrosion tests in acid solutions, we decided to perform similar studies with high-strength steel 70S2KhA (Table 5). This steel is prone to hydrogen charging in 2 M HCl, but its hydrogen charging is considerably smaller in 2 M H₂SO₄. The reason lies in the fact that the corrosion rate of steel is rather high in the background 2 M H₂SO₄ solution, which results in the rapid removal of the metal surface layer where the content of absorbed hydrogen is the highest. As a result, the total hydrogen content in the samples is smaller.

Table 5. Effect of nitrogen-containing inhibitors (5.0 mM) on the corrosion and hydrogen charging of 70S2KhA steel in 2 M H₂SO₄ and 2 M HCl (25°C). The etching duration was 2 h.

Acid	Inhibitor	k , g/(m ² ·h)	Z_{cor} , %	$V_{\text{H}_2}^*$, cm ³ /100 g	Z_{H_2} , %
H ₂ SO ₄	–	35.3	–	2.76	–
	Catamine AB	9.2	73.9	1.33	51.8
	IFKhAN-92	0.71	98.0	0.06	97.8
HCl	–	11.4	–	4.62	–
	Catamine AB	6.36	44.2	1.72	62.6
	IFKhAN-92	0.59	94.8	0.56	87.2

* Data were adjusted for metallurgical hydrogen amount, which is 0.34 cm³/100 g steel.

Both CIs studied inhibit the corrosion and hydrogenation of 70S2KhA steel in solutions of mineral acids, but the degrees of protection are rather high only in the case of IFKhAN-92.

A qualitative relationship has been shown between the ability of CIs to reduce the rate of incorporation of cathodically evolved hydrogen into steel and its ability to prevent the hydrogen charging of the metal bulk during corrosion. It should be understood that we measured the rates of diffusion of cathodic hydrogen into steel under conditions as close as possible to the steady-state conditions. In contrast, the corrosion of metals usually occurs under conditions far from steady-state ones. In spite of these differences, it can be seen that the more strongly a CI slows down the penetration of hydrogen into steel, the more efficiently it inhibits the hydrogen charging of the metal during corrosion.

Comparison of the inhibitory effect of Catamine AB and IFKhAN-92 showed that IFKhAN-92 was more efficient both in inhibiting steel corrosion and in preventing its hydrogen charging. Previously, we noted a high protective effect and prevention of hydrogen charging by composite CIs based on IFKhAN-92 during the corrosion of low-carbon, high-strength, and chromium-nickel steels in acid media [79–82]. The results of the comparative study clearly demonstrate the great prospects of triazole derivatives for practical application in the protection of steels in solutions of mineral acids in comparison with QAS. Triazole

derivatives make it possible to achieve reliable steel protection not only against corrosion but also against hydrogen charging. QAS do not always show such outstanding results. The successful inhibition of hydrogen charging of steels by the triazole under study is largely determined by its ability to significantly slow down the penetration rate of hydrogen released on a steel surface into the metal bulk.

Conclusions

1. The kinetics of hydrogen evolution and incorporation into steels in solutions of sulfuric and hydrochloric acids has been studied. It has been shown that addition of nitrogen-containing inhibitors such as Catamine AB and IFKhAN-92 significantly inhibits the hydrogen evolution in H_2SO_4 and HCl solutions on cathodically polarized low-carbon steel 08kp. These compounds slow down both partial reactions of this process, *i.e.*, hydrogen molization on a steel surface and its incorporation into the metal bulk. IFKhAN-92 provides the strongest inhibition of these partial reactions.
2. Catamine AB and especially IFKhAN-92 are efficient CIs of low-carbon and high-strength steels in solutions of H_2SO_4 and HCl . Along with the inhibition of metal corrosion, these compounds can significantly reduce their hydrogen charging, which is largely due to a decrease in the rate of hydrogen penetration into the metal.
3. Comparison of the protective properties of the quaternary ammonium salt, Catamine AB, and a triazole derivative, IFKhAN-92, indicates the great prospects of using the triazole as a CI of steels in acid media. This additive not only strongly inhibits steel corrosion but also suppresses its hydrogen charging most efficiently.

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