Inhibition of steel corrosion in model stratum water containing acetic acid and saturated with H_2S and CO_2

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Abstract

The inhibitory composition, which is a solution of the reaction products of polyamines with carboxylic acids in an organic solvent was shown to have a high efficiency against corrosion of carbon steel in model stratum water containing CH_3COOH and saturated with H_2S and CO_2. The research was carried out using the methods of gravimetry, potentiodynamic polarization, impedance spectroscopy, and electrochemical diffusion techniques. At a concentration of 200 mg/L, the inhibitory composition reaches a protective efficiency of 87% in the presence of H_2S (400 mg/L) and CO_2 (1 excess atmosphere) in the model stratum water. With the introduction of 5–10% hydrocarbon phase into this medium under dynamic conditions, the protective effectiveness increases up to 97%. The analysis of polarization curves in the media studied showed that the inhibitory composition slows down the cathodic process. The values of the protective effectiveness of the inhibitor calculated on the basis of polarization curves and impedance spectroscopy are in satisfactory agreement with the results obtained from gravimetric data. The inhibitory composition effectively reduces the diffusion of hydrogen into the metal. Impedance spectroscopy data made it possible to evaluate the adsorption of the inhibitory composition, to calculate the degree of coverage of the steel surface, to establish the type of adsorption isotherm and to calculate the value of ΔG^0_{ads}. The experiment under autoclave conditions confirmed the high protective effectiveness of the inhibitory composition.

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Introduction

Stratum waters containing acetic acid and saturated with hydrogen sulfide and carbon dioxide pose a great danger to the metal equipment of the oil and gas complex. The corrosivity of such environments in relation to X65 carbon steel was studied in detail in [1] at 70°C in a flow of deionized water saturated with CO_2 (2 bar) and containing H_2S and CH_3COOH. It has been shown that the rate of carbon dioxide corrosion doubles in the presence of 1000 ppm undissociated acetic acid. The introduction of small amounts of H_2S (0.004 bar) into the specified carbon dioxide environment reduces the corrosion rate of steel by 2 orders of magnitude due to the formation of a thin film of mackinawite on the surface. Corrosion is uniform. At higher H_2S concentrations, the surface FeS film cracks due to internal stress and uneven corrosion occurs. The addition of 1000 ppm free acetic acid to the H_2S/CO_2 solution eliminates the positive effects of low amounts of H_2S and increases the rate of corrosion, which becomes localized when pitting occurs. The authors of [2] also note that the introduction of CH_3COOH into H_2S/CO_2 environments at elevated temperatures (55–85°) leads to increased general and local corrosion of carbon steel. It was shown in [3] that the presence of CH_3COOH causes a change in the composition of corrosion products and the formation, along with mackinawite, of the cubic form of FeS. The combination of iron sulfides with different crystal structures in corrosion products causes the formation of a less dense film with reduced barrier properties. The authors of [4] note that mackinawite is not capable of providing a protective effect under dynamic test conditions due to its low adhesion to the steel surface and the possibility of being carried away by the flow of the medium.

The most common method of protecting metal equipment against corrosion is the use of inhibitors. It is known that the presence of hydrogen sulfide leads to the adsorption of sulfide and hydrosulfide ions on the surface of steel, which promotes the adsorption of a number of inhibitors. However, according to [5], in some cases, competitive adsorption occurs on the steel surface between iron sulfide and the inhibitor, which reduces its protective properties.

An important property of the inhibitor is the ability to reduce hydrogenation of the metal along with slowing down corrosion. In [6], it is indicated that in oil wells containing hydrogen sulfide, the oil itself can inhibit the hydrogenation process. The study of slowing down the flow of hydrogen diffusion into steel in hydrogen sulfide-containing environments is considered in [7]. Schiff bases are considered as inhibitors. The work was carried out in a two-phase liquid consisting of white spirit and an aqueous electrolyte containing 0.25 g/L CH_3COOH and 5 g/L NaCl. It has been shown that the presence of carbon dioxide does not increase the hydrogen adsorbability of steel, but does affect the effectiveness of the inhibitors. In accordance with the data of [8], in some cases, emulgin (a mixture of higher primary and secondary aliphatic amines – up to 99%, the rest is paraffin hydrocarbons) almost completely suppresses the diffusion of hydrogen into carbon steel in weakly acidic hydrogen sulfide-containing solutions. Previously, we showed the protective effectiveness of an inhibitory composition, which is a solution of nitrogen-containing compounds (polyamines) in a mixture of organic solvents, in relation to carbon steel in simulated stratum waters containing CO_2, H_2S and CH_3COOH [9]. In inhibited solutions in the presence of all three corrosion stimulants, a lower rate of steel corrosion and a higher protective effect of the inhibitory composition are observed than in the absence of CO_2.

The purpose of this work is to study the effectiveness of an inhibitory composition in relation to corrosion and hydrogenation of St3 carbon steel in simulated stratum water containing acetic acid and saturated with H_2S and CO_2.

Experimental

The inhibitory composition, which is a solution of the reaction products of polyamines with carboxylic acids in an organic solvent, was provided for research by Gazprom VNIIGAZ LLC.

Gravimetric and electrochemical measurements were carried out on samples of St3 steel with composition, mass.%: C – 0.2; Mn – 0.5; Si – 0.15; P – 0.04; S – 0.05; Cr – 0.30; Ni – 0.20; Cu – 0.20; Fe – 98.36.

Model stratum water MW2 of composition, g/L: Na_2SO_4 – 1.4703, $CaCl_2 \cdot 2H_2O$ – 21.1974, $MgCl_2$ – 1.6393, NaCl – 73.1014, CH_3COOH – 0.25 was used, into which hydrogen sulfide (400 mg/L) and carbon dioxide (1 excess atmosphere) were introduced.

Gravimetric corrosion tests at room temperature and 80°C for 24 hours and 1 hour, respectively, were carried out under static conditions. A number of experiments were performed in a two-phase system “hydrocarbon phase – MW2 + H_2S (400 mg/L) (1:9)” under dynamic conditions (~240 rpm). Diesel fuel was used as the hydrocarbon phase. In another embodiment, the two-phase system had the composition “white spirit – MW2 (1:5)” with continuous flow of H_2S and stirring. In these cases, the duration of the experiment was 6 hours.

In parallel, tests were carried out in the same model stratum water MW2 in an autoclave (at partial pressures of CO_2 and H_2S of 0.8 and 1.5 MPa, respectively).

Polarization potentiodynamic (potential application rate 0.66 mV/s) curves were measured on the electrodes in the solutions under study in a three-electrode cell with separated anode and cathode spaces using an IPC-Pro MF potentiostat manufactured at the Institute of Physical Chemistry and Electrochemistry named after A.N. Frumkin RAS. Potentials were measured with respect to a saturated silver/silver chloride electrode and converted to the normal hydrogen scale. The counter electrode is smooth platinum.

Impedance spectra were studied in the frequency range ($\omega/2\pi$) of 10 kHz–0.05 Hz with an alternating voltage amplitude of 10 mV, using an electrochemical measuring complex from Solartron (UK) consisting of a 1255 SI impedance analyzer and a SI 1287 potentiostat. The results obtained were processed using a program ZView 3.0 that allows calculations for any equivalent circuits with up to 20 elements.

Before the experiments, the working electrodes were ground to class 6 cleanliness and degreased with acetone.

The protective effect of the inhibitory composition (25–200 mg/l) is calculated according to gravimetric corrosion tests, polarization and impedance measurements using the formulas

$$Z, \% = 100[(K_0 - K_{\mathrm{Inh}})/K_0)] \quad (1)$$

$$Z, \% = 100[(i_0 - i_{Inh})/i_0] \quad (2)$$

$$Z, \% = 100[(R_{p,Inh} - R_{p,0})/R_{p,Inh}], \quad (3)$$

where K_0 (i_0) and K_{Inh} (i_{Inh}) are the corrosion rates (current densities) in the absence and presence of an inhibitor in solution, respectively; $R_{p,Inh}$ and $R_{p,0}$ are the values of polarization resistance in a medium with and without an inhibitor, respectively, calculated on the basis of an equivalent impedance circuit. Corrosion current densities (i_0, i_{Inh}) were calculated by extrapolating the Tafel sections of the polarization curves to the corrosion potential. The polarization resistance was calculated using the formula

$$R_p = [R_1 \cdot (R_2 + R_D)]/(R_1 + R_2 + R_D), \quad (4)$$

where R_1 and R_2 are the charge transfer resistance in the anodic and cathodic reactions, respectively, R_D is the mass transfer resistance.

The study of the hydrogen diffusion through a steel membrane was carried out at room temperature according to the electrochemical diffusion technique. A two-chamber cell first proposed by Devanathan [10], separated by a steel membrane of 0.3 mm thick, with an area of 3.63 cm^2 was used. A working solution was introduced into the polarization part of the cell, and a precisely fixed volume of a titrated 0.01 N solution of potassium permanganate (40 ml) was introduced into the diffusion part (method developed by N.V. Kardash and V.V. Batrakov [11]). The duration of the experiments was 2 h at a corrosion potential. The amount of hydrogen diffused through the membrane was recalculated into electrical units (i_H). To characterize the effect of the inhibitor on the flow of hydrogen diffusion into the metal, the hydrogen penetration inhibition coefficient γ_H was used:

$$\gamma_H = i_{0,H} / i_H \quad (5)$$

where $i_{0,H}$ and i_H are the hydrogen diffusion currents in the absence and in the presence of an inhibitor in a solution ($\gamma > 1$ corresponds to a deceleration of diffusion, $\gamma < 1$ corresponds to acceleration, and $\gamma = 1$ – to the absence of an inhibitor effect).

Results and Discussion

In the presence of CO_2 (1 atm) in hydrogen sulfide-containing environments at room temperature, the corrosion rate, both in background and in inhibited solutions, is generally higher than in the absence of CO_2, and the protective effectiveness of the inhibitor is higher (Table 1).

At 80°C, like at room temperature, the corrosion rate both in the background solution and in the presence of an inhibitor is higher in the combined presence of H_2S and CO_2 compared to a solution without CO_2 (Table 2). However, the Z value of the inhibitory composition is lower at the two highest concentrations.

Table 1. Corrosion rate and protective effectiveness of the inhibitory composition in model stratum water saturated with H_2S and H_2S+CO_2, according to daily tests at room temperature.

c_{Inh}, mg/L	*K*, g/(m^2·h)		*Z*, %	
	H_2S	H_2S+CO_2	H_2S	H_2S+CO_2
0	0.3087	0.5719	–	–
25	0.2495	0.2925	19	48
50	0.2118	0.2256	31	61
100	0.1578	0.1804	49	68
200	0.1151	0.0761	63	87

Table 2. Corrosion rate and protective effectiveness of the inhibitory composition in model stratum water saturated with H_2S and H_2S+CO_2, at 80°C.

c_{Inh}, mg/L	*K*, g/(m^2·h)		*Z*, %	
	H_2S	H_2S+CO_2	H_2S	H_2S+CO_2
0	6.4324	9.2955	–	–
25	3.9148	5.4455	39	41
50	3.5172	4.5673	45	51
100	2.1103	4.1952	67	55
200	1.2408	2.8628	81	69

In a two-phase system with diesel fuel, the corrosion rates in background solutions containing H_2S and H_2S+CO_2 are close, but in the second case they are slightly higher, and in the presence of an inhibitor, on the contrary, they are significantly lower, which leads to higher *Z* values than in the presence of H_2S (Table 3). Apparently, in the presence of CO_2, better conditions are created for the adsorption of the components of the inhibitory composition. From the data presented it follows that the optimal inhibitor concentration is 200 mg/L.

Table 3. Corrosion rate of St3 steel and protective effectiveness of the inhibitor in a two-phase system with diesel fuel saturated with H_2S and H_2S+CO_2 under dynamic conditions.

c_{Inh}, mg/L	*K*, g/(m^2·h)		*Z*, %	
	H_2S	H_2S+CO_2	H_2S	H_2S+CO_2
0	3.2402	3.3697	–	–
25	2.3692	0.6328	27	81

c_{Inh}, mg/L	*K*, g/(m^2·h)		*Z*, %	
	H_2S	H_2S+CO_2	H_2S	H_2S+CO_2
50	1.5211	0.4748	53	86
100	0.9814	0.3171	70	91
200	0.4197	0.1068	87	97

Figure 1 shows photographs of steel samples after corrosion tests, and Figure 2 shows SEM images of their surface.

Figure 1. Photographs of the surface of steel samples after daily exposure to a solution containing H_2S+CO_2, in the absence (a) and in the presence of an inhibitory composition (200 mg/L) (b).

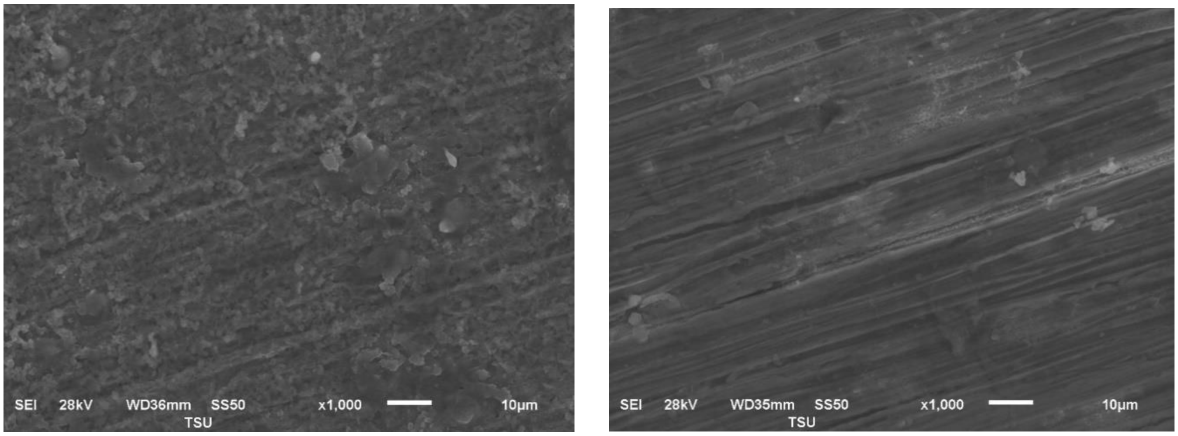
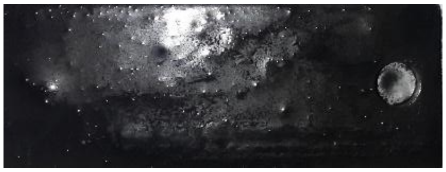


Figure 2. SEM images of a steel surface after daily exposure to a solution containing H_2S+CO_2, in the absence (a) and in the presence (b) of an inhibitory composition.

Corrosion tests carried out in parallel in an autoclave and in a two-phase system with white spirit at room (25°C) temperature and 80°C showed similar results in terms of corrosion aggressiveness and effectiveness of the inhibitor composition (Table 4).

Table 4. Results of corrosion tests of the inhibitory composition under static conditions of an autoclave and in a dynamic two-phase system with white spirit in an H_2S-containing environment.

***t*, °C**	**c_{Inh}, mg/L**	**Test type**		
		Autoclave		**Dynamic**
		Sample appearance	**K, g/(m^2·h)**	**K, g/(m^2·h)**
25	0	 	0.71	0.65
80			0.47	3.88
25	100		0.01	0.03
80			0.04	0.33
25	200		0.02	–
80			0.04	0.25

An increase in temperature under the same conditions affects hydrogen sulfide corrosion in different directions (Table 4). Under static conditions of an autoclave test, with an increase in temperature from 25 to 80°C, the corrosion rate even decreases from 0.71 to 0.47 g/(m^2·h). This is due precisely to the lack of dynamics, which allows the formation of a more effective protective layer of hydrogen sulfide corrosion products. A sixfold increase in corrosion rate with increasing temperature was shown to have in laboratory dynamic tests. In addition, at 80°C, the corrosion rate in the absence of an inhibitor is significantly higher in laboratory dynamic tests (3.88 g/(m^2·h)) than under static autoclave conditions (0.47 g/(m^2·h)). It is known [12, 13] that the movement of the test medium greatly accelerates internal corrosion, including in hydrogen sulfide environments. This is due to the fact that the dynamic factor will contribute to both the removal of corrosion products from the surface of the steel and the delivery of corrosive reagents to it. Therefore, studies of deposits on steel formed during internal corrosion processes play an important role in understanding the mechanisms of their occurrence and factors influencing this [14]. Table 4 shows the appearance of the sample with a film of sediment formed on it. The presence of CH_3COOH in the test environment affects the composition and rate of formation of hydrogen sulfide corrosion products [3, 15]. The occurrence of corrosion and the diffusion of hydrogen into steel depend on their composition and stability. The initial stage of the corrosion process is important, because a sediment layer is formed and local defects may appear [4, 16]. It is known that mackinawite is one of the first forms formed during hydrogen sulfide corrosion of steel, which, due to its polymorphism, then undergoes a number of transformations depending on test conditions. Despite the fact that under some conditions FeS can somewhat reduce the rate of internal corrosion [17], most studies show [18, 19] that mackinawite is formed porous and has low protective properties.

It was previously established [3] that the presence of CH_3COOH in H_2S-containing media promotes the formation of two forms of iron sulfide: tetragonal FeS (mackinawite) and cubic FeS. It will be difficult for such corrosion products (FeS with different edges) to form a continuous layer on the steel surface.

It can be seen (Table 4) that blistering with the formation of many bubbles is observed on the surface of steel samples after autoclave tests. This confirms that intense hydrogenation of steel samples occurred during the corrosion process [4, 20]. The analysis shows that other authors [21, 22] also observed a high intensity of coupled electrochemical processes of hydrogen sulfide corrosion, which led to hydrogenation of steel and its anodic dissolution. The corrosion rate of steel samples was shown to have the 1.1 g/(m^2·h) value in hydrogen sulfide-containing environments of the Astrakhan deposit [21].

Despite the fact that under static autoclave conditions when dosing the inhibitor into the aqueous phase, the corrosion rate turned out to be low (0.01–0.04 g/(m^2·h)), the inhibitor concentration of 100 mg/L was insufficient to provide protection against local hydrogen sulfide attack. As can be seen (Table 4), individual point damage is observed on the steel surface at 80°C. Further dosage doubling of the inhibitory reagent made it possible to eliminate the localization of corrosion on steel at a temperature of 80°C.

The results show (Table 4) that under dynamic test conditions at 25°C, the inhibitor protects against hydrogen sulfide corrosion even at a concentration of 100 mg/L. However, when the temperature rises to 80°C, a concentration of at least 200 mg/L is required for a more effective reduction in the corrosion rate.

Potentiodynamic polarization curves measured at room temperature in the solutions under study are shown in Figures 3 and 4. The cathodic process involves H^+ ions formed due to the dissociation of acetic acid, and also, according to [1], the reduction of undissociated CH_3COOH and H_2S molecules occurs:

$$2CH_3COOH + 2e \leftrightarrow 2CH_3COO^- + H_2$$

$$2H_2S + 2e \leftrightarrow H_2 + 2HS^-$$

Undissociated H_2CO_3 molecules formed as a result of CO_2 hydration can also be reduced, but their amount is insignificant, according to the ratio $[CO_2]/[H_2CO_3]=296$ [9]. The dissociation of H_2CO_3 and H_2S is suppressed due to the presence of stronger acetic acid. A comparison of polarization curves measured on a steel electrode in background solutions with H_2S and H_2S+CO_2 shows that in the presence of CO_2, inhibition of the cathodic process and facilitation of the anodic reaction are observed when E_{corr} shifts towards more negative potentials (Figures 3 and 4). This determines the peculiarities of the corrosion process.

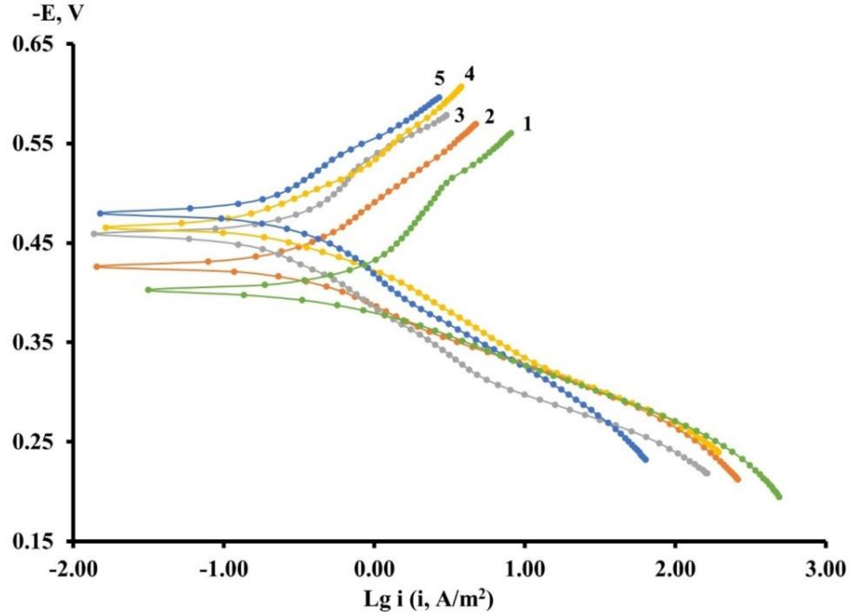


Figure 3. Polarization curves measured on a steel electrode in model stratum water saturated with H_2S in the absence of (1) and in the presence of inhibitory composition, mg/L: 2 – 25, 3 – 50, 4 – 100, 5 – 200.

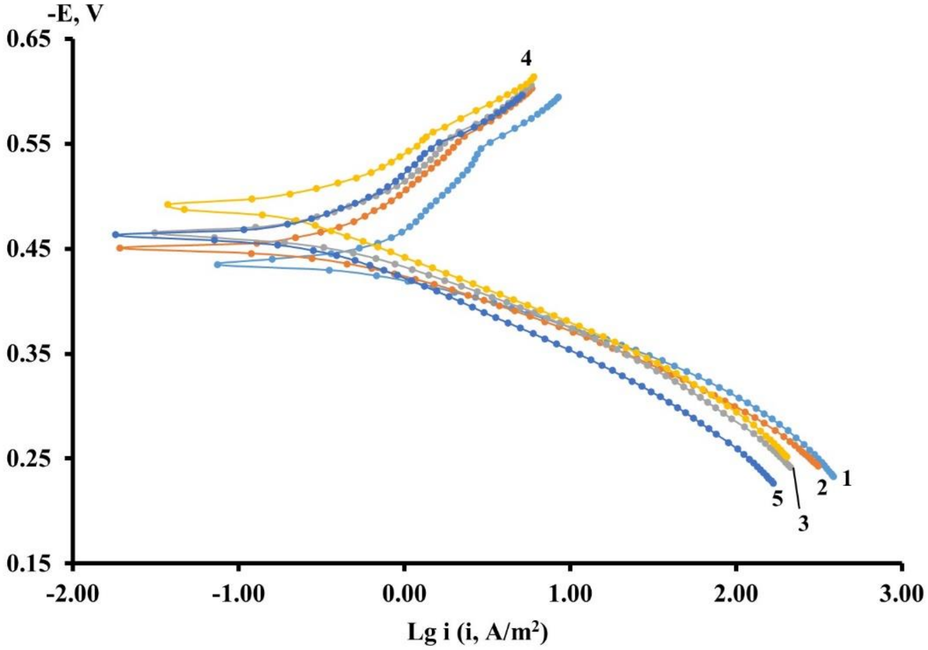


Figure 4. Polarization curves measured on a steel electrode in model stratum water saturated with H_2S+CO_2 in the absence of (1) and in the presence of inhibitory composition, mg/L: 2 – 25, 3 – 50, 4 – 100, 5 – 200.

From Figures 3 and 4 it follows that in the presence of an inhibitory composition both in a solution saturated with H_2S and in a solution with the simultaneous presence of CO_2 and H_2S, a slowdown in the cathodic process is observed with a shift in the corrosion potential (E_{corr}) towards negative values. Data on the protective effectiveness of the inhibitor, calculated on the basis of the polarization curves, are given in Table 5 for an environment saturated with CO_2 and H_2S.

Table 5. Kinetic parameters of the St3 steel electrode in solution saturated with H_2S+CO_2 in the absence and in the presence of the inhibitory composition and its protective efficiency (Z, %)

c_{Inh}, mg/L	$-E_{\mathrm{corr}}$, V	i_{corr}, A/m²	b_a, V	b_c, V	Z, %
0	0.45	0.56	0.043	0.150	–
25	0.45	0.18	0.048	0.150	68
50	0.46	0.16	0.054	0.150	71
100	0.49	0.13	0.061	0.145	77
200	0.46	0.12	0.059	0.140	78

From Table 5 it follows that there is a satisfactory convergence of the protective effectiveness of the inhibitor with the data obtained on the basis of daily gravimetric corrosion tests. The same picture is observed for the solutions containing only H_2S.

The results of impedance studies at E_{corr} are shown in Figures 5 and 6.

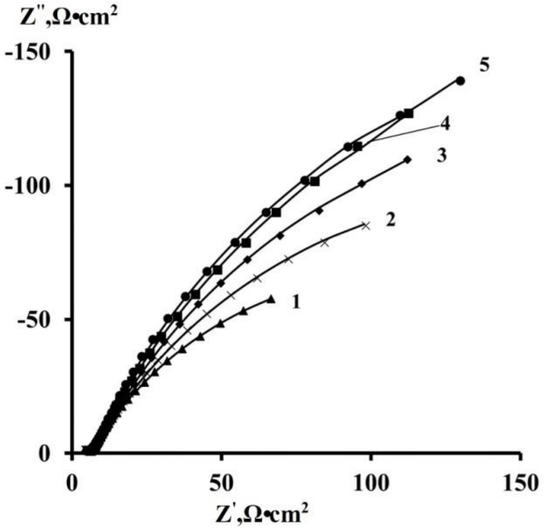


Figure 5. Nyquist diagram of a steel electrode in the MW2 solution saturated with H_2S at E_{corr} in the absence (1) and in the presence of the inhibitory composition, mg/L: 2 – 25, 3 – 50, 4 – 100, 5 – 200. The dots correspond to the experimental data, whereas the solid lines correspond to the impedance spectra fitted using the equivalent circuit.

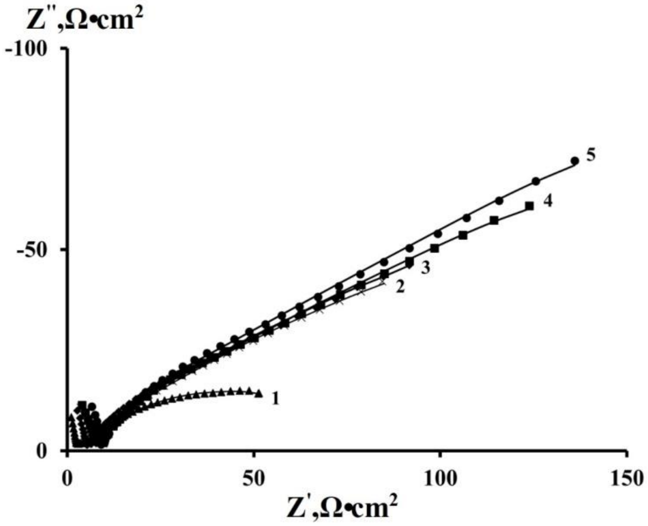


Figure 6. Nyquist diagram of a steel electrode in the MW2 solution saturated with H_2S+CO_2 at E_{corr} in the absence (1) and in the presence of the inhibitory composition, mg/L: 2 – 25, 3 – 50, 4 – 100, 5 – 200. The dots correspond to the experimental data, whereas the solid lines correspond to the impedance spectra fitted using the equivalent circuit.

From the Nyquist diagrams shown in Figures 5 and 6, it follows that the diameter of the arcs increases with the introduction of the inhibitory composition and an increase in its concentration. This indicates an increase in the total resistance in the system and, consequently, a decrease in the corrosion rate. The impedance measurement results were processed in accordance with the equivalent circuit shown in Figure 7, using the ZView 3.0 program, which allows calculations using any equivalent circuits with up to 20 elements.

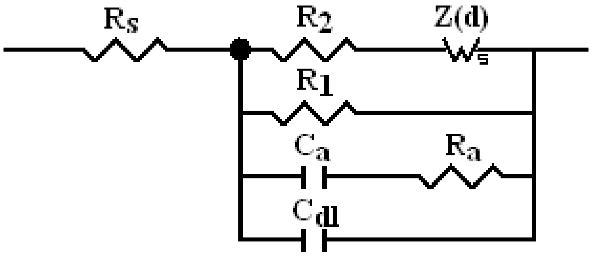


Figure 7. Equivalent circuit simulating the behavior of a steel electrode in the solutions under study.

Table 6 shows the numerical values of the elements of the equivalent circuit for a solution saturated simultaneously with CO_2 and H_2S.

Table 6. Numerical values of elements of the equivalent circuit at E_{corr} of the steel electrode in MW2 solution, saturated with H_2S+CO_2.

Element	**Concentration of inhibitory composition, mg/L**				
	Background	**25**	**50**	**100**	**200**
R_s, Ω·cm^2	1	2.7	3.6	3.9	6.5
C_a, μF/cm^2	40.1	253.7	164.2	152.4	223.6
R_1, Ω·cm^2	77.8	281.7	312.7	458.1	597.6
C_{dl}, μF/cm^2	38.1	25.7	17.9	12.8	10.5
R_2, Ω·cm^2	2.4	3.1	4.1	4.1	2.1
R_a, Ω·cm^2	78.8	9.3	11.7	17.4	8.1
R_d, Ω·cm^2	346.3	420.1	473	532.2	565.8
τ_d, s	27.7	41.2	41.7	51.8	53.1
p_d	0.47	0.43	0.42	0.40	0.40
S, %	4.7	3.3	3.7	3.7	3.7
R_p	63.61	155.95	188.89	247.07	291.19
Z, %	–	59.2	66.3	74.3	78.2

From Table 6 it follows that the charge transfer resistance in the cathodic reaction R_2 is significantly less than the mass transfer resistance R_D. This indicates the reduction of the depolarizer with a predominance of diffusion restrictions. The polarization resistance R_p increases with increasing concentration of the inhibitory additive, and the protective effectiveness calculated on its basis is in satisfactory agreement with the results obtained from gravimetric and polarization measurements. The same picture is observed for the MW2 solution containing only H_2S.

With increasing concentration of the inhibitory composition, a decrease in the capacitance of the electrical double layer C_{dl} is observed, indicating the adsorption of the components of the inhibitory additive. This makes it possible to calculate the steel surface coverage with the components of the inhibitory composition in the solutions under study using the formula [9]:

$$\Theta=(C_0-C)/(C_0-C_1) \tag{5}$$

where C_0, C and C_1 are the capacitances of the electric double layer in the solution without addition of inhibitory composition, with that and with the maximum coverage of the electrode surface with the adsorbed particles, respectively. The value of C_1 is calculated graphically based on the linear dependence $C_{\mathrm{dl}}=f(1/c_{\mathrm{Inh}})$ [9] and is equal to 8 μF/cm^2. The values of Θ calculated using formula (5) for various concentrations of the inhibitory additive are given below:

c_{Inh}	**25**	**50**	**100**	**200**
Θ	0.41	0.67	0.84	0.92

To select the isotherm that governs the adsorption of the components of the inhibitory composition, the graphical dependences of Θ *vs*. $\log c$, $\ln[c(1-\Theta)/\Theta]$ *vs*. Θ and c/Θ *vs*. c, corresponding to the Temkin ($Bc=\exp(f\Theta)$), Frumkin ($Bc=[\Theta/(1-\Theta)]\exp(-2a\Theta)$) and Langmuir ($c/\Theta=1/B+c$) isotherms are considered (Figure 8), where f is the parameter of the energy heterogeneity of the metal surface, B is the constant of adsorption equilibrium, a is the attraction constant characterizing the interaction between adsorbed particles, c is the concentration of the inhibitor.

From Figure 8 it follows that the best agreement with the rectilinear dependence is observed for the Frumkin isotherm. The segment cut off on the vertical axis allows us to calculate the value of B, which turned out to be equal to 0.016 L/mg. The value of B enables us to calculate the value of free adsorption energy according to the formula (6):

$$\Delta G_0^{\mathrm{ads}}=-RT\ln(B\cdot 10^6) \tag{6}$$

where 10^6 is the concentration of water in the solution, mg/L.

The value $-\Delta G_0^{\mathrm{ads}}$ at a temperature of 298 K is 24 kJ/mol. It can be assumed that the adsorption of the components of the inhibitory composition is due to physical forces with a certain amount of chemisorption.

Studies of the influence of the inhibitory composition on the diffusion of hydrogen formed during metal corrosion through a steel membrane showed a significant slowdown in the penetration of hydrogen into the metal (Table 7).

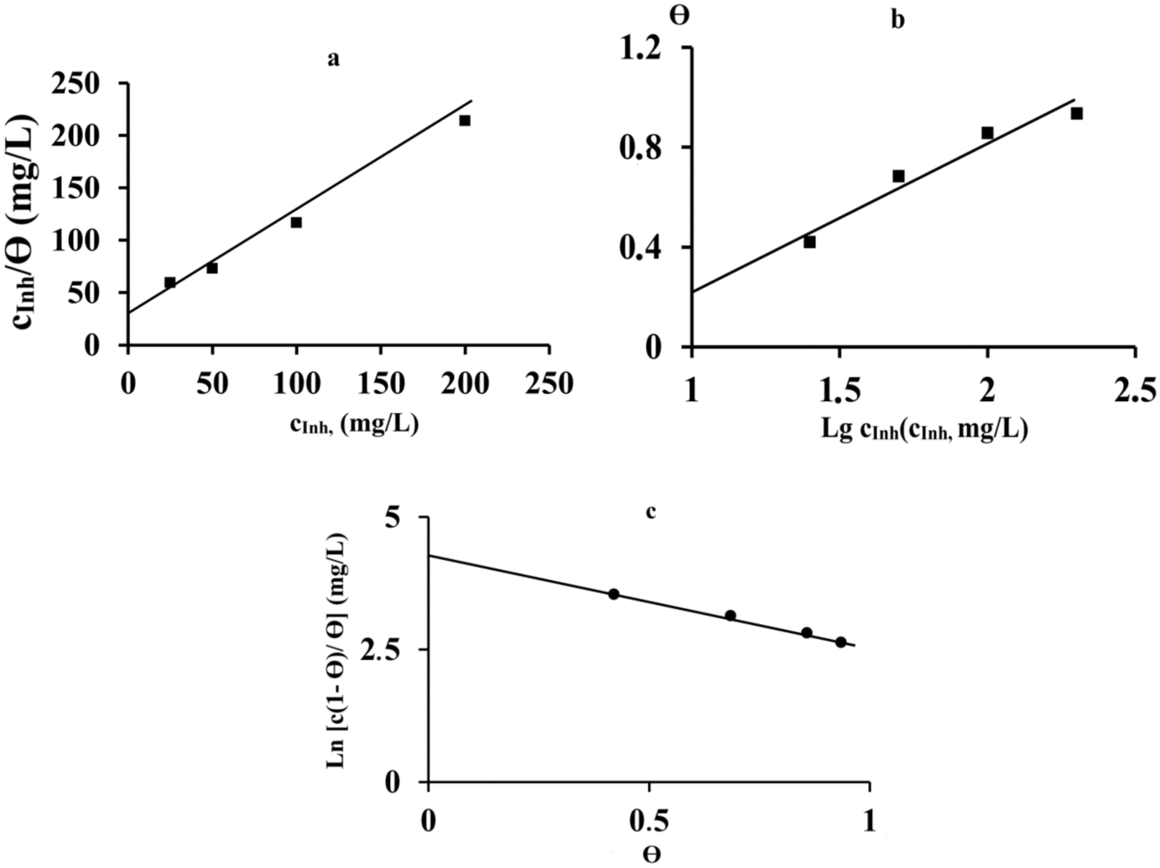


Figure 8. Adsorption isotherms for St3 steel in MW2 media saturated with H_2S+CO_2.

Table 7. The influence of the inhibitor on the diffusion current of hydrogen through a steel membrane in the MW2 medium containing 400 mg/L H_2S, and its inhibition coefficient γ_H.

c_{Inh}, mg/L	i_H, A/m^2	γ_H
0	0.8062	–
25	0.5256	1.53
50	0.3809	2.11
100	0.2418	3.33
200	0.1619	4.98

The most significant reduction in the diffusion of hydrogen into steel is observed at a concentration of the inhibitory composition of 200 mg/L.

It should be noted that data on the preservation of steel ductility (to control hydrogenation) measured under laboratory and autoclave test conditions in parallel with corrosion rate confirmed that the inhibitor is also capable of protecting against the penetration of hydrogen into steel.

Conclusion

The protective effectiveness of a composition consisting of reaction products of polyamines with carboxylic acids in an organic solvent against the corrosion of St3 steel in model stratum water MW2 containing CH_3COOH and saturated with H_2S and CO_2 was studied by the methods of gravimetry, potentiodynamic polarization and impedance spectroscopy.

According to daily gravimetric tests at room temperature, the protective effectiveness of the inhibitor at a concentration of 200 mg/L reaches 87% in the presence of H_2S and CO_2. In the presence of hydrocarbon phase under dynamic conditions, the protective effectiveness increases. The experiment under autoclave conditions confirmed the high protective effectiveness of the inhibitory composition. The inhibitory composition significantly slows down the penetration of hydrogen into steel in simulated stratum water containing H_2S.

According to polarization studies, the inhibitory composition slows down the cathodic process both in the presence of H_2S and in the presence of H_2S+CO_2 in model stratum water. Impedance spectroscopy data confirmed the protective effectiveness of the inhibitory composition and made it possible to determine its adsorption on steel and to calculate the change in the free energy of adsorption equal to –24 kJ/mol.

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