Anti-corrosion protection of carbon steel with lidocaine in hydrogen sulfide-containing environments

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Abstract

In the past decade, active researches of expired drugs as inhibitors of metal corrosion are being conducted in various aggressive environments. In this work, the inhibitory effect of the expired drug Lidocaine was studied against corrosion of carbon steel in NACE and M1 model stratum waters of oil and gas fields containing 400 mg/L H_2S.The concentration of the drug varied within 20–80 mg/L. The protective effect (Z) of Lidocaine (80 mg/L) is 81% and 86%, according to daily gravimetric tests, respectively, in NACE and M1 media. At 80°C, the Z value increases to 85% and 95%, respectively. An analysis of the polarization curves in the media under study showed that Lidocaine slows down the cathode process in the NACE+H_2S medium and both partial electrode reactions in M1+H_2S. According to impedance spectroscopy data, the surface coverage of the electrode by the inhibitor was calculated. The adsorption of Lidocaine follows the Langmuir isotherm. A value of the free energy of adsorption indicates the physical nature of the drug adsorption.

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Introduction

Hydrogen sulfide corrosion is one of the most serious causes of corrosive destruction of metal equipment in oil and gas complexes. In most cases, the high aggressiveness of the exploited environments is explained by the presence of natural and associated petroleum gases, oil, as well as hydrocarbon condensate, the presence of moisture and aggressive components such as H_2S and CO_2 [1–3]. To combat corrosion destruction, the use of corrosion inhibitors is considered the most effective and economical [4]. However, the use of organic corrosion inhibitors is limited due to increasing environmental legislation worldwide. Expired drugs are the most important alternative candidates for protecting metals against corrosion. Their use for this purpose has been studied for more than a decade. Many researchers refer to them as “green” inhibitors. Expired drugs are considered environmentally friendly, biodegradable, and economical due to their low cost. There is another reason for using expired drugs as metal corrosion inhibitors. The fact is that a huge number of expired drugs, including antibiotics, are released into the environment and are found in large quantities in soils and especially in the aquatic environment. Antibiotics slow down the growth of algae, harm beneficial bacteria and other aquatic organisms [5].

Among the various anthropogenic sources of pollution, waste dumps for the pharmaceutical industry and other municipal solid waste often appear due to leachate seepage [6]. Many healthcare facilities dispose of expired drugs together with household waste. Solid and semi-solid pharmaceuticals are disposed of by incineration/pyrolysis, encapsulation and burial in special landfills, while wastewater treatment plants are recommended for liquid pharmaceutical waste. The environmental friendliness and safety of these methods are currently being studied [7]. The use of drugs as corrosion inhibitors helps to solve the problem of their disposal. The effectiveness of drugs is determined by the presence of heteroatoms (O, N, S, *etc.*), unsaturated bonds, and aromatic rings in their molecules. These features are also characteristic of organic inhibitors with high protective effectiveness. In [8], the inhibitory effect of the expired drug Omeprazole against corrosion of carbon steel in a model stratum water containing hydrogen sulfide was studied. The concentration of the inhibitor varied within 10–60 mg/L. At the maximum concentration, Omeprazole exhibits a protective effect of 80% at room temperature. The inhibitor causes a slowdown in both partial electrode reactions. Adsorption of the drug on the steel surface is described by the Langmuir isotherm. The calculated value of the free energy of adsorption indicates chemisorption of the inhibitor. In [9], penicillin was used as a corrosion inhibitor for low-carbon steel in Na_2SO_4 solution with pH=3 containing 15 ppm of hydrogen sulfide. The penicillin molecule contains heteroatoms of oxygen, nitrogen, and aromatic rings. Gravimetric tests and potentiodynamic polarization have shown that the effectiveness of the inhibitor increases with increasing penicillin concentration. At a concentration of 500 ppm at 25°C, the protective effect of penicillin is 94.2% and decreases with increasing temperature up to 45°C. The authors accept without proof the blocking mechanism of action of the inhibitor, while demonstrating a change in the apparent activation energy of the process upon introduction of the inhibitor into the medium. According to the authors, the adsorption of penicillin on steel obeys the Langmuir isotherm.

The aim of this work is to investigate the protective properties of the expired drug Lidocaine in relation to carbon steel in model stratum waters typical for oil and gas production environments containing 400 mg/L H_2S.

Experimental

Electrochemical measurements and corrosion tests were carried out on carbon steel St3 of composition, wt.%: 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 in model stratum waters NACE (g/L: NaCl – 5; CH_3COON – 0.25) and M1 (simulation of stratum water of the Samotlor oil field with the content, g/L: NaCl – 17; $CaCl_2$ – 0.2; $MgCl_2 \cdot 6H_2O$ – 0.2; $NaHCO_3$ – 0.8) saturated with H_2S (400 mg/L).

The duration of the gravimetric tests was 24 hours at room temperature and 30 minutes at 80°C. The steel samples (30×20×3 mm) were polished to grade 6 purity and degreased with acetone before the experiments.

Electrochemical measurements were performed in a three-electrode plastic cell after 15 minutes exposure of the working electrode in solution. The potentials were measured relative to a saturated silver/silver chloride electrode and recalculated to the standard hydrogen scale. The counter electrode was smooth platinum. Potentiodynamic polarization measurements were performed using an IPC-Pro potentiostat at a potential scan rate of 0.66 mV/s. Impedance measurements and their analysis were carried out according to [8].

The protective effect of the inhibitor was calculated according to gravimetric tests, polarization and impedance measurements using the formulas:

$$Z,\% = \frac{\left(K_0 - K_{\text{inh}}\right)}{K_0} \cdot 100 \tag{1}$$

$$Z,\% = \frac{\left(i_0 - i_{\text{inh}}\right)}{i_0} \cdot 100 \tag{2}$$

$$Z,\% = \frac{\left(R_{\text{p,inh}} - R_{\text{p,0}}\right)}{R_{\text{p,inh}}} \cdot 100 \tag{3}$$

where K_0 (i_0) and K_{inh} (i_{inh}) are the rate (current density) of corrosion in the absence and presence of an inhibitor in solutions, respectively, $R_{\text{p,inh}}$ and $R_{\text{p,0}}$ are the values of polarization resistance in a medium with and without an inhibitor, respectively, calculated on the basis of an equivalent impedance circuit using the formula:

$$R_{\text{p}} = \frac{R_1\left(R_2 + R_{\text{d}}\right)}{\left(R_1 + R_2 + R_{\text{d}}\right)} \tag{4}$$

where R_1 and R_2 are the charge transfer resistances in the anode and cathode reactions, respectively, and R_{d} is the mass transfer resistance.

The corrosion current densities were calculated by extrapolating the Tafel sections of the polarization curves to the corrosion potential.

The expired drug Lidocaine (2-(diethylamino)-*N*-(2,6-dimethylphenyl)acetamide) was used as an inhibitor. As a medicine, the drug has an antiarrhythmic effect. The structural formula of the drug is shown in Figure 1. The concentration of the inhibitor varied in the range of 20–80 mg/L.

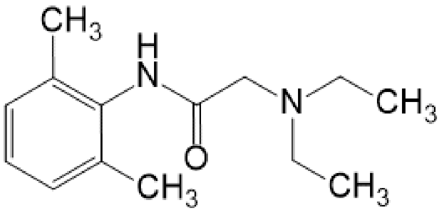

Figure 1. The structural formula of Lidocaine.

Results and Discussion

Figure 2 shows the polarization curves obtained in a NACE+400 mg/L H_2S solution, and Table 1 shows the kinetic parameters calculated on their basis.

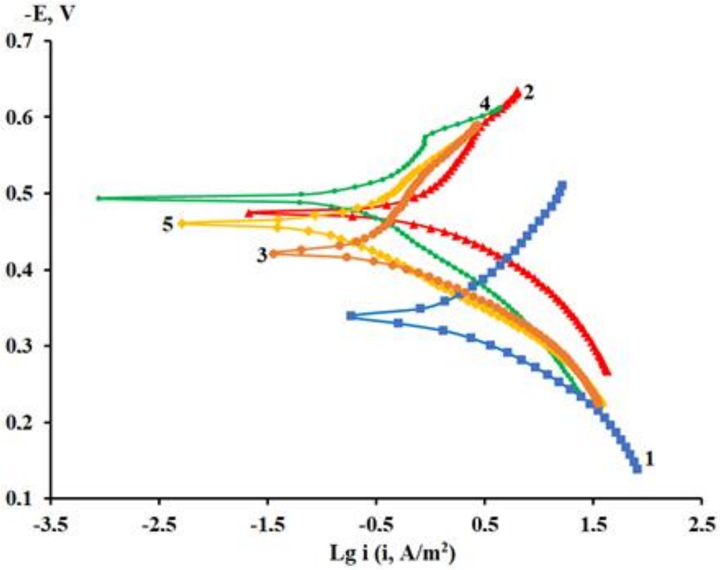

Figure 2. Polarization curves of a steel electrode measured in NACE+400 mg/L H_2S medium in the absence of (1) and in the presence of Lidocaine, mg/L: 2 – 20, 3 – 40, 4 – 60, 5 – 80.

Table 1. Kinetic parameters of a steel electrode in a NACE+400 mg/L H_2S solution in the absence and presence of Lidocaine and its protective effect (*Z*,%).

c_{inh}, mg/L	$-E_{corr}$, V	i_{corr}, A/m^2	b_a, V	b_c, V	*Z*, %
0	0.35	0.62	0.060	0.100	–
20	0.49	0.34	0.062	0.120	45
40	0.43	0.10	0.055	0.120	83
60	0.40	0.07	0.050	0.100	88
80	0.45	0.05	0.055	0.100	92

The slope coefficients of the Tafel sections of the anode polarization curves are 0.050–0.060 V, and the cathode ones are close to 0.100–0.120 V. It can be seen from the Figure 2 that Lidocaine causes inhibition of the cathode process in this medium. As its concentration increases, the corrosion current density decreases, reaching a minimum value at 80 mg/L, which determines a protective effect of 92% (Table 1).

The polarization curves measured on a steel electrode in a solution of M1+400 mg/L H_2S in the absence and in the presence of Lidocaine additives are shown in Figure 3.

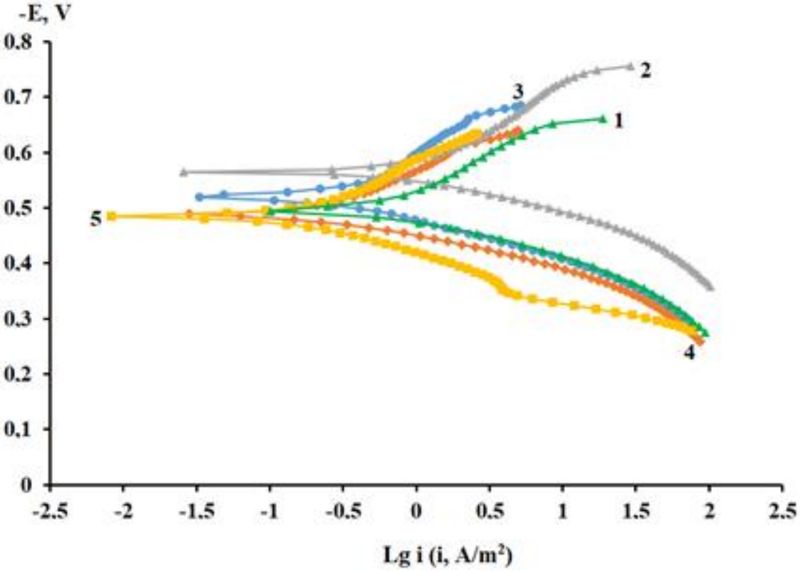

Figure 3. Polarization curves of a steel electrode in M1+ 400 mg/L H_2S medium in the absence of (1) and in the presence of Lidocaine, mg/L: 2 – 20, 3 – 40, 4 – 60, 5 – 80.

It follows from the Figure 3 that Lidocaine in M1 medium causes a slowdown in the cathodic process at all concentrations studied and the anode process at 60 and 80 mg/L. The Tafel slope coefficients of the cathode curves are close to 0.110 V, and the anode slope coefficients are close to 0.060 V, slightly increasing for the two highest concentrations of the inhibitor (Table 2). The protective effect of the inhibitor increases with increasing its concentration, reaching 90% at 80 mg/L.

Table 2. Kinetic parameters of a steel electrode in M1+400 mg/L H_2S solution in the absence and presence of Lidocaine and its protective effect (*Z*,%).

c_{inh}, mg/L	$-E_{corr}$, V	i_{corr}, A/m^2	b_a, V	b_c, V	*Z*, %
0	0.50	0.49	0.060	0.095	–
20	0.55	0.32	0.060	0.110	36
40	0.52	0.15	0.060	0.110	68
60	0.50	0.15	0.070	0.110	75
80	0.50	0.05	0.080	0.110	90

The results of 24-hour corrosion tests of carbon steel in the solutions studied and the magnitude of the protective effects of the inhibitor are shown in Table 3.

Table 3. Corrosion rate of steel in NACE+400 mg/L H_2S and M1+400 mg/L H_2S media and protective effect of Lidocaine, according to daily gravimetric corrosion tests at room temperature.

C_{inh}, mg/L	*K*, g/(m²·h)		*Z*, %	
	NACE+H_2S	M1+H_2S	NACE+H_2S	M1+H_2S
0	0.653	0.245	–	–
20	0.317	0.130	52	47
40	0.220	0.083	66	67
60	0.189	0.077	71	68
80	0.125	0.033	81	86

The protective effect of the inhibitor increases with an increase in Lidocaine concentration in the media studied. Already at a concentration of 20 mg/L in the NACE medium, *Z* is 52%, while in the M1 medium the protective effect is slightly lower. A further increase in the concentration to a maximum value of 80 mg/L leads to *Z* values equal to 81% and 86%, respectively. A comparison of the protective effects calculated from corrosion and polarization tests shows a qualitative agreement, and some discrepancies in numerical values are obviously related to the different duration of the experiment.

Corrosion tests at 80°C have shown that the protective effectiveness of Lidocaine in both NACE+H_2S and M1+H_2S solutions is higher than at room temperature (Table 4).

Table 4. Corrosion rate and protective effect of Lidocaine in NACE+400 mg/L H_2S and M1+400 mg/L H_2S media according to the results of gravimetric tests at 80°C. The exposure time is 0.5 hours.

c_{inh}, mg/L	*K*, g/(m²·h)		*Z*, %	
	NACE+H_2S	M1+H_2S	NACE+H_2S	M1+H_2S
0	22.12	12.62	–	–
20	19.06	10.44	14	17
40	17.31	6.80	22	46
60	4.701	0.95	79	92
80	3.410	0.64	85	95

The protective effectiveness of Lidocaine in the media studied is confirmed by the results of impedance measurements. Figures 4 and 5 show Nyquist diagrams of a steel electrode in the solutions under study. The diameter of semicircles in a Nyquist diagram increases with the introduction of the inhibitor 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. This is consistent with the results obtained on the basis of polarization curves and gravimetric tests.

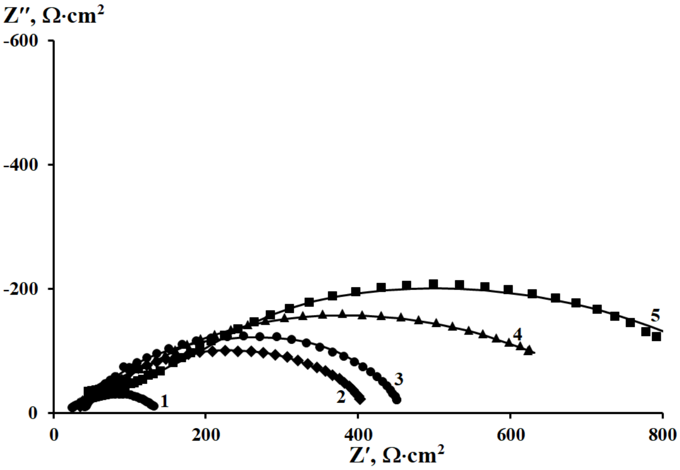

Figure 4. Nyquist diagram for a steel electrode in a NACE+400 mg/L H_2S medium in the absence of (1) and in the presence of Lidocaine, mg/L: 2 – 20, 3 – 40, 4 – 60, 5 – 80. The dots correspond to the experimental data, whereas the solid lines correspond to the impedance spectra fitted using the equivalent circuit.

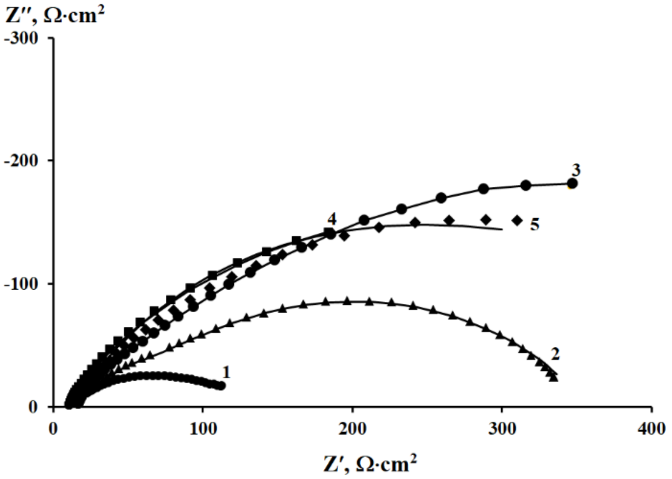

Figure 5. Nyquist diagram for a steel electrode in M1+400 mg/L H_2S medium in the absence of (1) and in the presence of Lidocaine, mg/L: 2 – 20, 3 – 40, 4 – 60, 5 – 80. The dots correspond to the experimental data, whereas the solid lines correspond to the impedance spectra fitted using the equivalent circuit.

The analysis of impedance hodographs was carried out using an equivalent circuit, according to [8]. Table 5 shows the numerical values of the elements of the equivalent circuit in a solution of NACE+400 mg/L H_2S. It can be seen that the charge transfer resistance in the anode reaction R_1 increases with the introduction and increase of Lidocaine concentration, indicating an inhibition of the anode reaction on steel. The mass transfer resistance R_d is significantly higher than the charge transfer resistance in the cathode reaction

R_2, indicating the reduction of the depolarizer with a predominance of diffusion limitations. The polarization resistance R_p increases with increasing concentration of the inhibitory additive, and the protective effect calculated on its basis is in satisfactory agreement with the results obtained from gravimetric and polarization measurements.

Table 5. Numerical values of the elements of the equivalent circuit at E_{corr} of the steel electrode in the NACE medium containing 400 mg/L H_2S and additives of the inhibitor.

Element	**Background**	**Lidocaine concentrations, mg/L**			
		20	**40**	**60**	**80**
R_s, Ω·cm^2	23.0	32.7	37.5	39.4	44.1
C_{dl}, μF/cm^2	45.7	19.6	15.9	13.3	2.3
R_1, Ω·cm^2	117.0	385.9	424.5	697.3	907.1
R_2, Ω·cm^2	27.0	117.8	131.1	125.4	84.1
C_a, μF/cm^2	16.4	6.0	5.8	11.6	2.6
R_d, Ω·cm^2	6670	20148	23923	21843	14988
p_d	0.6	0.6	0.6	0.5	0.6
τ_d, s	27.4	17.0	12.0	61.6	18.4
R_a, Ω·cm^2	63.4	211.7	176.7	255.7	654.6
Sum of sqr., %	2.0	2.6	1.9	3.1	1.7
R_p	114.9	378.8	417.1	675.8	855.6
Z, %	–	69.6	72.4	82.9	86.5

The numerical values of the elements of the equivalent circuit in M1+400 mg/L H_2S solution are shown in Table 6. The change in R_1 with the introduction and increase in Lidocaine concentration is similar to that observed in NACE+400 mg/L H_2S, as well as the ratio of R_2 and R_d indicates the predominance of diffusion limitations in the cathode process. The values of the protective effect calculated according to the polarization resistance R_p increase with an increase in the inhibitor concentration, that is consistent with the results of gravimetric and polarization measurements.

The capacitance of the double electric layer C_{dl} decreases with the introduction of Lidocaine and an increase in its concentration in both solutions under study, indicating its adsorption on the surface of the steel electrode. This makes it possible to calculate the electrode surface coverage θ with an inhibitor using the formula:

$$\theta = \frac{(C_0 - C)}{(C_0 - C_1)} \tag{5}$$

where C_0, C and C_1 are the capacitances of the electric double layer in the solution without addition of an inhibitor, with that and with the maximum coverage of the electrode surface with the adsorbed inhibitor particles, respectively.

Table 6. Numerical values of the elements of the equivalent circuit at E_{corr} of the steel electrode in the M1 medium containing 400 mg/L H_2S and additives of the inhibitor.

Element	Background	Lidocaine concentrations, mg/L			
		20	40	60	80
R_s, Ω·cm^2	11.4	17.3	16.6	14.0	3.9
C_{dl}, μF/cm^2	28.1	6.2	3.0	2.4	1.9
R_1, Ω·cm^2	124.3	206.2	380.2	412.8	559.0
R_2, Ω·cm^2	6.8	4.5	2.6	58.4	9.7
C_a, μF/cm^2	60.3	28.0	40.0	14.7	30.5
R_d, Ω·cm^2	960.2	1760	3035	3159	3421
p_d	0.5	0.6	0.6	0.6	0.6
τ_d, s	14.4	55.2	24.0	15.3	10.7
R_a, Ω·cm^2	104.0	113.0	63.0	20.1	17.2
Sum of sqr., %	5.2	1.4	1.5	0.2	1.2
R_p	110.1	184.6	337.9	365.8	480.7
Z, %	–	40.4	67.5	69.9	77.1

The value of C_1 was calculated graphically based on the linear dependence $C_{dl}=f(1/c_{inh})$ [8] and was equal to 2.32 and 0.5 μF/cm^2 for the NACE and M1 media, respectively. The steel surface coverage with Lidocaine, depending on its concentration in the media under study, is shown in Table 7.

Table 7. The values of the electrode surface coverage θ in NACE+400 mg/L H_2S and M1+400 mg/L H_2S media.

c_{inh}, mg/L	20	40	60	80
θ in NACE	0.60	0.69	0.75	0.99
θ in M1	0.79	0.91	0.93	0.95

To select an isotherm corresponding to the data given in Table 7, it was checked their correspondence to the Temkin isotherm $Bc=\exp(f\cdot\theta)$, the Frumkin isotherm $Bc=[\theta/(1-\theta)]\exp(-2a\theta)$ and the Langmuir isotherm $c/\theta=1/B+c$, where f is the factor of the energy inhomogeneity of the surface, B is the constant of adsorption equilibrium, a is the attraction constant characterizing the interaction between adsorbed particles, and c is the concentration of the inhibitor. For this purpose, the graphical dependences of θ *vs* ($\ln c$), $\ln[c(1-\theta)/\theta]$ *vs* θ and c/θ *vs* c were considered, corresponding to the Temkin, Frumkin, and Langmuir isotherms, respectively. The inhibitor concentration is expressed in mM.

It turned out that the best fitting of the data to the linear dependence corresponds to the Langmuir isotherm in both media (Figure 6).

Table 8 shows the numerical values of the approximation reliability calculated using the least squares method.

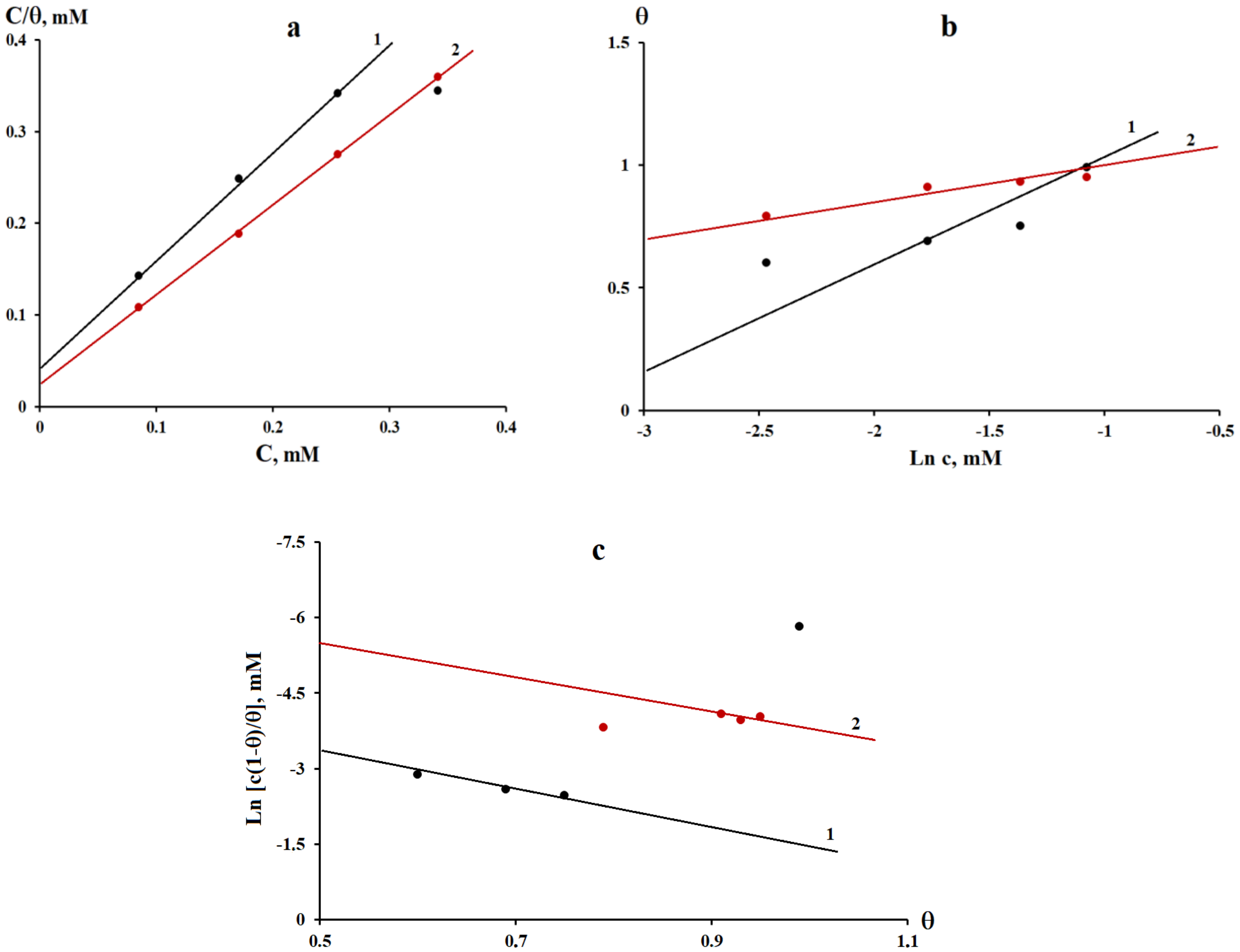

Figure 6. Adsorption isotherms for St 3 steel in NACE+400 mg/L H_2S(1) and M1+400 mg/L H_2S(2) solutions with Lidocaine.

The segment cut off on the vertical axis of Figure 6a allows us to calculate the adsorption equilibrium constant *B*, which turned out to be $22.2 \cdot 10^3$ L/mol in the NACE medium and $43 \cdot 10^3$ L/mol in M1.

With a known value of *B*, the free energy of adsorption $-\Delta G^0_{\text{ads}}$ is calculated using the formula:

$$-\Delta G^0_{\text{ads}} = RT\ln\left(B\cdot 55.55\right)$$

where 55.55 is the concentration of water in mol/L.

The values of $-\Delta G^0_{\text{ads}}$ at a temperature of 298 K in NACE and M1 media amount to 34.7 and 36.4 kJ/mol, respectively. It can be assumed that Lidocaine adsorption is of a physical nature with a certain amount of chemisorption.

Table 8. Indicators of the accuracy of the approximation.

Isotherm	**Accuracy of the approximation, R^2**	
	NACE	**M1**
Langmuir	0.892	0.999
Temkin	0.788	0.933
Frumkin	0.779	0.673

Conclusion

The protective effectiveness of the expired drug Lidocaine has been studied against corrosion of carbon steel in model stratum waters NACE and M1 containing 400 mg/L H_2S.

The protective effect of Lidocaine (80 mg/L) is 81% and 86%, according to daily gravimetric tests in NACE and M1 media, respectively. At 80°C, the Z value increases to 85% and 95%, respectively.

Analysis of the polarization curves showed that Lidocaine causes inhibition of the cathode process in NACE+400 mg/L H_2S solutions and both partial electrode reactions in M1+400 mg/L H_2S media. The data of impedance spectroscopy indicate a decrease in the capacitance of the double electric layer with an increase in the concentration of the drug. This made it possible to calculate the electrode surface coverage θ with an inhibitor, determine the type of adsorption isotherm, and calculate the free energy of adsorption.

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References

1. C. Rena, Corrosion behavior of oil tube steel in simulant solution with hydrogen sulfide and carbon dioxide, *Mater. Chem. Phys.*, 2005, **93**, no. 2–3, 305–309. doi: 10.1016/j.matchemphys.2005.03.010

2. R.K. Vagapov, Study of Hydrogenation and Corrosion of Steel Equipment and Pipelines at the Production Facilities of H_2S-Containing Hydrocarbon Raw Materials, *Inorg. Mater. Appl. Res.*, 2022, **13**, no. 6, 1658–1665. doi: 10.1134/S2075113322060302
3. R.R. Kantyukov, D.N. Zapevalov and R.K. Vagapov, Assessment of the Effect of Operating Conditions on the Resistance of Steels Used in H_2S-Containing Environments at Hydrocarbon Production Facilities, *Metallurgist*, 2022, **65**, 1369–1380. doi: 10.1007/s11015-022-01284-4
4. B. Obot, M.M. Solomon, S.A. Umoren, R. Suleiman, M. Elanany, N.M. Alanazi and A.A. Sorour, Progress in the development of sour corrosion inhibitors: Past, present, and future perspectives, *J. Ind. Eng. Chem.*, 2019, **79**, 1–18. doi: 10.1016/j.jiec.2019.06.046
5. H. Sun, J. Yang, Y. Wang, Y. Liu, C. Cai and A. Davarpanah, Study on the Removal Efficiency and Mechanism of Tetracycline in Water Using Biochar and Magnetic Biochar, *Coatings*, 2021, **11**, no. 11, 1354. doi: 10.3390/coatings11111354
6. Z. Zhang, D. Zhou, J. He, Y. He, C. Yu, Y. Long, D. Shen, J. Yao and H. Chen, Insight into the impact of industrial waste co-disposal with MSW on groundwater contamination at the open solid waste dumping sites, *Chemosphere*, 2023, **344**, 140429. doi: 10.1016/j.chemosphere.2023.140429
7. B. Sapkota and A. Pariatamby, Pharmaceutical waste management system – Are the current techniques sustainable, eco-friendly and circular? A review, *Waste Manage.*, 2023, **168**, 83–97. doi: 10.1016/j.wasman.2023.05.052
8. L.E. Tsygankova, V.A. Bryksina, O.V. Alekhina and N.V. Shel, Protective efficacy of Omeprazole against hydrogen sulfide corrosion of carbon steel, *Theory and Practice of Corrosion Protection*, 2022, **27**, no. 4, 36–44 (in Russian). doi: 10.31615/j.corros.prot.2022.106.4-4
9. A.M. Farimani, H. Hassannejad, A. Nouri and A. Barati, Using oral penicillin as a novel environmentally friendly corrosion inhibitor for low carbon steel in an environment containing hydrogen sulfide corrosive gas, *J. Nat. Gas Sci. Eng.*, 2020, **77**, 103262. doi: 10.1016/j.jngse.2020.103262

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