New inhibitors based on substituted 1,2,4-triazoles for mild steel in hydrochloric acid solutions

M.D. Plotnikova,* A.D. Solovyev, A.B. Shein, A.N. Bakiev
and A.S. Sofronov

Perm State National Research University, st. Bukireva 15, 614068 Perm, Russian
Federation

*E-mail: plotnikova-md@mail.ru

Abstract

The article presents the results of studies on triazole derivatives as corrosion inhibitors for mild steel in hydrochloric acid solutions of various concentrations, namely, 1 M and 5 M. 5-Heptyl-1,2,4-triazole-3,4-diamine and 4,5-diphenyl-4*H*-1,2,4-triazole-3-thiol were studied. Grimme's semi-empirical GFN2-xTB method was used to calculate the protonation of the investigated molecules in hydrochloric acid media. Weight loss tests were carried out on steel C1018 at a temperature of 293 K with an exposure time of 24 h. The polarization curves in the temperature range of 293–353 K were recorded in the potentiodynamic mode in a three-electrode cell from the cathodic to the anodic potentials at a potential sweep rate of 0.5 mV/s, using a SOLARTRON 1280C electrochemical measuring complex. It was found that 5-heptyl-1,2,4-triazole-3,4-diamine at a concentration of 200 mg/L has the greatest inhibition effect in 1 M HCl, whereas 4,5-diphenyl-4*H*-1,2,4-triazole-3-thiol is most efficient in 5 M HCl at the same concentration. It was determined by the potentiodynamic polarization method that the investigated compounds are cathodic-type inhibitors. The effective activation energy of the corrosion process in the presence of 4,5-diphenyl-4*H*-1,2,4-triazole-3-thiol decreases, which indicates that chemisorption on the electrode surface occurs. The degrees of surface coverage of the steel with triazole molecules were calculated based on the results of electrochemical impedance spectroscopy at the corrosion potential. It was found that the adsorption process obeys the Freundlich equation for an energetically inhomogeneous surface.

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1. Introduction

Corrosion of metals and alloys causes great economic and environmental damage [1]. Specially selected inhibitors are used [2–4] to reduce the destruction of metals. When added to a corrosive environment in low concentrations, they slow down the corrosion rate without a significant change in the composition of the corrosive media.

Now the development of new non-toxic corrosion inhibitors that do not contain heavy metals and inorganic phosphates is of great importance [5, 6]. Many organic compounds

containing heteroatoms are able to reduce the corrosion of metals in acidic solutions. Inhibitors based on nitrogen-containing compounds are most widespread [7, 8]. These compounds include thiols, thiosulfonic acids, thiophenes, and sulfur-containing triazoles [9, 10].

Thus, the purpose of this work was to study the efficiency of triazole derivatives as potential corrosion inhibitors of C1018 steel in solutions of hydrochloric acid of various concentrations.

Experimental

2.1. Synthesis of inhibitors

Figure 1. Synthesis of 5-heptyl-1,2,4-triazole-3,4-diamine.

At the first stage, 2-amino-5-heptyl-1,3,4-thiadiazole was synthesized from octanoic acid and thiosemicarbazide. In detail, octanoic acid was mixed with thiosemicarbazide, POCl_3 was added dropwise, then the mixture was heated and basified with sodium hydroxide to give the corresponding 2-amino-1,3,4-thiadiazole. Further, 2-amino-5-n-heptyl-1,3,4-thiadiazole was condensed with hydrazine hydrate to give 5-heptyl-1,2,4-triazole-3,4-diamine.

^1H NMR (400 MHz, DMSO-d_6) δ 0.87–0.90 (t, 3H, $J = 6.7$ Hz, CH_3), 1.29–1.41 (m, 8H, $\text{CH}_2-(\text{C}_4\text{H}_8)$), 1.69–1.76 (q, 2H, $J = 7.4$, $-\text{CH}_2-\text{CH}_2\text{N}$), 2.88–2.92 (t, 2H, $J = 7.6$, NCH_2), 5.17 (s, 4H, NH_2). ^{13}C NMR (400 MHz, DMSO-d_6) δ 14.30, 22.87, 29.17, 29.23, 29.97, 30.71, 31.95, 162.53, 167.83.

Figure 2. Synthesis of 4,5-diphenyl-4H-1,2,4-triazole-3-thiol.

Benzoyl hydrazide was prepared by the reaction of benzoyl chloride with hydrazine hydrate in CH_2Cl_2 at room temperature overnight. The reaction of benzoyl hydrazide with phenyl isothiocyanate in ethanol under reflux for 3 h gave the corresponding 1-benzoyl-4-phenyl-3-thiosemicarbazide. The resulting thiosemicarbazide was cyclized in aqueous sodium hydroxide to give 1,2,4-triazole-3-thiol.

^1H NMR (400 MHz, DMSO-d_6) δ 13.27 (s NH), 7.51–7.58 (m, 4H, Ph), 7.37–7.42 (dd, $J = 7.9$ Hz, 4H, Ph), 7.20–7.24 (t, $J = 7.8$ Hz, 1H, Ph), 6.89–6.92 (t, $J = 7.3$ Hz, 1H, Ph). ^{13}C NMR (400 MHz, DMSO-d_6) δ 165.4, 148.1, 140.0, 132.6, 129.3, 129.2, 128.7, 128.4, 121.2, 117.7.

2.2. Quantum chemical calculations

The presence of nitrogen atoms in the molecules of CP-20 and CP-38 inhibitors gives them basic properties in aqueous solutions. A semi-empirical calculation was performed using the GFN2-xTB Grimm method [11, 12] to determine the protonation sequence of individual atoms taking implicit solvation in an aqueous medium into account.

2.3. Weight loss measurements

Samples of mild steel C1018 with the composition, wt.%: Fe – 98.27; C – 0.20; Mn – 0.50; Si – 0.30; P – 0.04; S – 0.04; Cr – 0.15; Ni – 0.30; Cu – 0.20, were used in the study. The experiments were carried out in 1 M and 5 M HCl solutions prepared from distilled water and 37% HCl. Organic synthesis products – triazole derivatives – were used as the corrosion inhibitors (Table 1).

Table 1. Triazoles studied in this work as corrosion inhibitors.

Code	Formula	Name according to nomenclature
CP-20	<chem>CCCCCCC1=NC(=N)C(N)=N1</chem>	5-heptyl-1,2,4-triazole-3,4-diamine
CP-38	<chem>c1ccc(cc1)-c2nc(cc2S)-c3ccccc3</chem>	4,5-diphenyl-4H-1,2,4-triazole-3-thiol

The main parameters of C-steel corrosion were evaluated according to generally accepted methods [13]. Weight loss tests were carried out using rectangular plates made of C1018 steel with a size of $25 \times 20 \times 2$ mm. The working surface area was 1180 mm^2 .

The corrosion rates (K) and the degree of protection (Z_{WL}) were calculated using the equations:

$$K = \frac{m_0 - m}{S \cdot \tau};$$

$$Z_{WL} = \frac{K_0 - K}{K_0} \cdot 100\%,$$

where m_0 is the mass of the initial sample, g; m is the mass of the sample after corrosion testing and removal of corrosion products, g; S is the surface area of the sample, m²; τ is the immersion time, h; K_0 and K are the corrosion rates of steel, respectively, in the pure solution and with addition of an inhibitor, in g/(m²·h).

2.4. Electrochemical measurements

A Solartron 1280C measuring complex (Great Britain) consisting of an impedance analyzer SI 1255 and a potentiostat SI 1287 and a three-electrode cell with separate cathode and anode spaces were used for electrochemical studies.

The polarization curves were recorded by the potentiodynamic technique from the cathodic to the anodic region at a scanning rate of 0.5 mV/s. All the potentials are presented in the silver chloride electrode scale.

Polarization measurements were carried out in the temperature range from 293 to 353 K. The cell was connected with a LOIP LT 100 thermostat with external circulation to maintain the required temperature.

Before each electrochemical experiment, the surface of the electrode was cleaned with sanding paper and then degreased with acetone.

The method of polarization curves allows one to calculate the corrosion rate (i_{corr}) in current density units, the corrosion potential (E_{corr}), and to determine the type of the inhibitor, *i.e.* which of the partial electrode reactions (hydrogen evolution or metal ionization) is mainly hindered by the inhibitor. This method also allows one to determine the Tafel sections of the polarization curves and calculate the degree of protection from electrochemical data [14]:

$$Z_{\text{el}} = \frac{i_0 - i_{\text{inh}}}{i_0}$$

where i_0 and i_{inh} are the current densities of steel corrosion, respectively, in the pure solution and with addition of an inhibitor, in A/m².

Based on the electrochemical results the activation energy of the corrosion process was calculated. The calculations were performed by the temperature-kinetic method. The effect of temperature on the current density in cases of concentration polarization or delayed discharge stage is described by an equation similar to the Arrhenius equation [15]:

$$\ln i = \frac{-E_{\text{ef}}}{RT}$$

Where i is the corrosion current density, A/m²; E_{ef} is the effective activation energy of the corrosion process, J/mol; T is the temperature, K.

A straight line in the $\lg i = f(1/T)$ coordinates allows E_{ef}/R to be calculated as the slope.

The surface coverage (θ) of the C1018 electrode by corrosion inhibitor was determined from the equation:

$$\theta = \frac{C_0 - C}{C_0 - C_1}$$

Where C_0 , C and C_1 are, respectively, the capacitance of the double electric layer in the pure acid solution, in the solution with a given concentration of the inhibitors, and in the solution with $\theta = 1$. The value of C_1 was determined by extrapolating the curve in coordinates $C = f(1/C_{\text{inh}})$ to $(1/C_{\text{inh}}) = 0$, where C_{inh} is the concentration of the inhibitor in the solution, mg/L.

All the data presented in this work was obtained by averaging the results of three parallel measurements. MS Excel software was used to calculate the average results and standard deviations of direct and indirect measurements.

3. Results and Discussion

According to the results of quantum chemical calculations, protonation of CP-20 occurs at the first and second stages by the nitrogen atoms of triazole; protonation of amino groups is possible only at the third and fourth stages, and protonation of the amino group at the C11 carbon atom of the triazole ring is the least energetically favorable (Figure 3).

Protonation of CP-38 is possible in two stages. A tautomer with a protonated nitrogen atom of the N₂ triazole ring is more stable in a neutral molecule. It is interesting that, according to the results of the calculations, at the next stage of protonation the form with a protonated sulfur atom S₁₂ and another nitrogen atom N₃ of the triazole cycle is more stable (Figure 4).

The results of weight loss experiments in the presence of the compounds studied in 1 M and 5 M HCl solutions are presented in Table 2.

According to the results obtained (Table 2), the inhibition effect of CP-38 tends to increase with an increase in concentration of acid, unlike CP-20. The greatest inhibitory effect in 1 M HCl belongs to CP-20 at a concentration of 200 mg/L ($Z = 92.5\%$), and in 5 M HCl to CP-38 at the same concentration ($Z = 94.9\%$). The protective effect of both inhibitors increases with an increase in their concentration in solution from 50 to 200 mg/L.

When comparing the results of weight loss experiment and quantum chemical calculations, it can be assumed that the growth in the protective properties of CP-38 molecules is caused by the conjugation of π -electrons of benzene rings as substituents in 3-substituted 1,2,4-triazole. The presence of the second type of heteroatoms (S) in the CP-

38 molecule also contributes to the greater molecule basicity and ability to adsorb on the steel surface.

Figure 3. Structures optimized at the level of theory GFN2-xTB[GBSA(H₂O)] geometries of neutral CP-20 molecule and its protonated forms.

Figure 4. Structures optimized at the level of the theory GFN2-xTB[GBSA(H₂O)] geometries of the neutral molecule CP-38, its mono- and diprotonated form.

Table 2. Results of weight loss experiments on mild steel in solutions of hydrochloric acid in the presence of triazoles.

Chiper	C_{inh} , mg/L	1 M HCl		5 M HCl	
		K , g/m ² ·h	Z_{wl} , %	K , g/m ² ·h	Z_{wl} , %
—	—	2.51±0.13	—	15.89±0.79	—
CP-20	50	0.32±0.01	87.2±2.6	13.51±0.54	15.0±0.6
	100	0.25±0.01	89.9±2.4	13.50±0.47	15.0±0.5
	200	0.19±0.01	92.5±3.7	12.64±0.57	20.4±0.8
CP-38	50	0.31±0.01	87.7±3.0	2.91±0.15	84.8±4.2
	100	0.28±0.01	88.8±2.7	1.78±0.05	90.7±2.7
	200	0.22±0.01	91.1±3.1	0.97±0.04	94.9±3.8

Figures 5 and 6 show the polarization curves of C1018 steel in hydrochloric acid solutions with various concentrations, without and with addition of the triazole inhibitors.

Figure 5. Polarization curves of C1018 steel in 1 M HCl containing 100 mg/L of the triazoles at 293 K. **Figure 6.** Polarization curves of C1018 steel in 5 M HCl containing 100 mg/L of the triazoles at 293 K.

The compounds studied are cathodic-type inhibitors [17]. The corrosion currents in the inhibited solutions decrease in comparison with the currents in hydrochloric acid solutions for CP-20 in 1 M HCl, CP-38 in 1 M and 5 M HCl. There are no results for CP-20, since according to electrochemical measurements, this compound has no inhibitive properties. The corrosion potential is shifted to the cathodic region.

The protective effect of the studied compounds is calculated from the polarization data obtained (Table 3).

Table 3. Corrosion-electrochemical characteristics of C1018 in hydrochloric acid solutions with various concentrations with addition of 100 mg/L of the inhibitors at various temperatures.

Code	<i>T</i> , K	1 M HCl		5 M HCl	
		$i_{\text{corr}} \cdot 10^5$, A/cm ²	Z_{el} , %	$i_{\text{corr}} \cdot 10^5$, A/cm ²	Z_{el} , %
–	293	7.67±0.38	–	58.44±1.75	–
	303	8.00±0.24	–	75.63±1.51	–
	313	8.34±0.33	–	116.28±3.37	–
	333	13.94±0.49	–	186.14±7.45	–
	353	52.75±2.89	–	1165.90±23.32	–
CP-20	293	1.83±0.05	76.1±2.3	44.91±1.34	23.2±0.9
	303	2.26±0.05	71.8±1.4	60.26±1.81	20.3±0.8
	313	3.00±0.08	64.0±1.6	92.87±2.79	20.1±1.1
	333	6.45±0.32	53.7±2.7	148.31±4.45	20.3±1.2
	353	14.30±0.43	72.9±2.2	966.95±29.01	17.1±0.9
CP-38	293	1.19±0.05	84.5±3.8	5.75±0.12	90.2±2.3
	303	2.04±0.10	74.5±3.7	6.21±0.19	91.8±2.3
	313	2.35±0.12	71.8±2.9	11.75±0.28	89.9±3.6
	333	3.08±0.10	77.9±3.0	15.23±0.61	91.8±2.8
	353	7.77±0.25	85.3±2.7	117.93±4.72	89.9±3.6

Comparison of the results presented in Table 3 shows that the corrosion rate increases with an increase in temperature, and the compounds studied exhibit a high protective effect throughout the temperature range used. The exception is CP-20 in 5 M HCl solution, which correlates with gravimetric tests.

The retention of protective properties of inhibitors studied in the temperature range of 293–353 K indicates that a chemisorption process takes place between their molecules and the steel surface. However, according to the activation energy values presented in Table 4, a decrease in the E_a values in the presence of CP-38 confirms the fact of the chemisorption process on the steel surface [18]. The activation energy values of the corrosion process in the presence of CP-20 approximately coincide with the E_a values in the pure acid. This can probably be explained by the presence of competitive adsorption of ions in the corrosive media and inhibitor molecules [19].

Table 4. The values of the activation energy of the corrosion process without and in the presence of 100 mg/L triazoles.

Code	E , kJ/mol	
	1 M HCl	5 M HCl
—	26.4 ± 1.3	40.5 ± 2.0
CP-20	25.9 ± 1.0	41.0 ± 1.9
CP-38	18.0 ± 0.9	24.1 ± 1.2

The impedance spectra of C1018 steel in HCl solutions at the corrosion potential E_{corr} are a combination of semicircles of one capacitive arc in the high frequency region and an additional capacitive arc in solutions of 1 M HCl or inductive arc in solutions of 5 M HCl in the low frequency region. In Figures 7–9, ReZ is the real component of the impedance and $-ImZ$ is the imaginary component of the impedance.

Figure 7. Impedance spectra of C1018 steel in a solution of 1 M HCl at E_{corr} with addition of various concentrations of CP-20. **Figure 8.** Impedance spectra of C1018 steel in a solution of 1 M HCl at E_{corr} with addition of various concentrations of CP-38.

Figure 9. Impedance spectra of C1018 steel in a solution of 5 M HCl at E_{corr} with addition of various concentrations of CP-38.

The addition of the inhibitors to the system causes an increase in the diameter of the capacitive semicircle in the high frequency region, the greater the higher the inhibitor concentration, which is probably due to the hindrance of the electrode reactions.

The equivalent electrical circuit shown in Figure 10 was used to simulate the corrosion-electrochemical behavior of C1018 steel in a solution of 1 M HCl in the presence of inhibitors. In this circuit: R_s is the solution resistance; R_1 is the resistance equal to $(R_a \cdot R_c)/(R_a + R_c)$, where R_a is the resistance of the anodic process (metal dissolution) and R_c is the resistance of the cathodic process (evolution of hydrogen); the resistance R_2 and the capacitance C_1 reflect the adsorption of an intermediate of the anodic process; CPE_1 is a constant phase element describing the capacitance of a double electric layer on an inhomogeneous surface of a solid electrode.

The behavior of the inhibitor in 5 M HCl solution is satisfactorily described by the equivalent circuit in Figure 11. In this circuit: R_s , R_1 and CPE_1 have the same physical meaning as in the circuit in Figure 10, the resistance R_2 and the inductance L_1 describe the adsorption of an intermediate of the anodic process.

The values of the χ^2 parameter calculated in ZView2 for the circuits are in the range $(2-6) \cdot 10^{-4}$, which indicates a good correlation with the experimental data.

Figure 10. Equivalent electrical circuit for steel C1018 in 1 M HCl solution at E_{corr} .

Figure 11. Equivalent electrical circuit for steel C1018 in 5 M HCl solution at E_{corr} .

The values of the parameters of the equivalent circuits (Figures 10 and 11) for C1018 steel in HCl solutions in the presence of inhibitors are given in Tables 5 and 6, respectively.

Table 5. Values of parameters of equivalent circuits for C1018 steel in 1 M HCl solution without and in the presence of inhibitors.

$C_{inh},$ mg/L	$R_1, \Omega \cdot \text{cm}^2$	$R_2, \Omega \cdot \text{cm}^2$	$CPE_1, \mu\text{F} \cdot \text{cm}^{-2} \cdot \text{s}^{(p-1)}$		$C, \mu\text{F}/\text{cm}^2$	θ
			Q	p		
–	294±11	863±32	36.52±1.43	0.86±0.01	–	–
CP-20						
10	261±9	461±12	22.10±0.99	0.90±0.01	3.18±0.19	0.88±0.01
50	423±13	983±38	17.71±0.87	0.89±0.01	2.83±0.21	0.96±0.01
100	541±20	1027±36	17.07±0.84	0.90±0.01	3.58±0.23	0.97±0.01
200	663±26	1633±62	16.07±0.86	0.91±0.01	3.19±0.19	0.98±0.01
CP-38						
10	460±14	810±39	10.16±0.51	0.95±0.01	2.05±0.11	0.97±0.01
50	846±31	1090±41	8.07±0.34	0.95±0.01	1.84±0.09	0.98±0.01
100	1044±41	1229±41	6.71±0.36	0.94±0.01	1.52±0.06	0.99±0.01
200	1543±65	5584±241	5.55±0.25	0.94±0.01	1.31±0.05	0.99±0.01

Table 6. Values of parameters of equivalent circuits for steel C1018 in 5 M HCl solution without and in the presence of inhibitor.

$C_{inh},$ mg/L	$R_1, \Omega \cdot \text{cm}^2$	$R_2, \Omega \cdot \text{cm}^2$	$CPE_1, \mu\text{F} \cdot \text{cm}^{-2} \cdot \text{s}^{(p-1)}$		$L, \text{H} \cdot \text{cm}^2$	θ
			Q	p		
–	53±3	181±5	3.16±0.15	0.87±0.01	–	–
CP-38						
10	63±2	574±14	1.93±0.07	0.84±0.01	135±7	0.59±0.01
50	304±9	3524±176	1.51±0.08	0.84±0.01	1546±62	0.81±0.01
100	307±11	4090±204	1.42±0.08	0.84±0.01	1989±71	0.98±0.01
200	352±9	5167±258	1.30±0.04	0.84±0.01	2532±101	0.99±0.01

It follows from Table 5 that there is a regular increase in the R_1 and R_2 resistances and a decrease in the Q parameter of the constant phase element CPE_1 (at comparable p values) with an increase in the concentration of the compounds studied. These correlations indicate the inhibition of the electrode processes (mainly the cathodic process) in the presence of the triazoles and their adsorption on the electrode surface. The R_2 and C_1 parameters, along with

the interpretation of the adsorption of the intermediate of the cathodic process, can also be associated with the kinetics of the adsorption of compounds on the electrode surface (the Frumkin-Melik-Gaikazyan impedance without a diffusion impedance).

The degrees of surface coverage of the electrode with the inhibitor molecules are approximated in the coordinates of the Langmuir and Freundlich equations [20] (Figure 12, Table 7).

Figure 12. Langmuir (a) and Freundlich (b) isotherms of adsorption of inhibitors in 1 and 5 M HCl solutions.

Table 7. Parameters of Langmuir and Freundlich isotherms for the adsorption of CP-20 and CP-38 on the surface of C1018 in HCl solutions.

Chiper	Langmuir			Freundlich		
	$K, \text{dm}^3/\text{g}$	$Q, \mu\text{mol} \cdot \text{m}^{-2}$	R^2	K	n	R^2
1 M HCl						
CP-20	0.8940	0.9791	0.9990	0.8251	0.0335	0.9989
CP-38	4.8540	0.9893	0.9987	0.9537	0.0074	0.9999
5 M HCl						
CP-38	0.1279	1.0154	0.9901	0.4089	0.1750	0.9903

The calculated correlation coefficients indicate that the process of surface coverage by the inhibitor molecules more accurately follows the Freundlich isotherm which describes adsorption on an energetically inhomogeneous surface.

Conclusions

- Triazole derivatives are effective inhibitors of acid corrosion of steel C1018 in 1 M and 5 M HCl solutions.

- According to the results of quantum chemical calculations, protonation of 5-heptyl-1,2,4-triazole-3,4-diamine occurs at the first and second steps only at the nitrogen atoms of the heterocycle, while in the case of 4,5-diphenyl-4*H*-1,2,4-triazole-3-thiol, protonation also involves the sulfur atom, which probably results in the retention of the protective effect in concentrated acids.
- The effective activation energy of the C1018 corrosion process in HCl solutions in the presence of 4,5-diphenyl-4*H*-1,2,4-triazole-3-thiol decreases. This fact indicates the formation of an inhibitor film by chemisorption on the steel surface, which creates diffusion restrictions.
- The inhibitors possess a cathodic effect. The open circuit potential of corrosion process shifts to the cathodic region.
- From analysis of the impedance spectra, the surface coverage of the electrode rises with an increase of the inhibitor concentration, thus improving protection.
- The Freundlich isotherm model better fits the adsorption process on an energetically inhomogeneous surface.

Conflict of Interests

The authors declare there is no conflict of interests.

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