

## Original articles

Research article

<https://doi.org/10.17308/kcmf.2022.24/9056>**Corrosion inhibition of steel by selected homologues of the class 3-alkyl-5-amino-1H-1,2,4-triazoles in acidic media**D. V. Lyapun, A. A. Kruzhilin<sup>✉</sup>, D. S. Shevtsov, Yu. V. Aseeva, Kh. S. Shikhaliev<sup>1</sup>Voronezh State University,  
1 Universitetskaya pl., Voronezh 394018, Russian Federation**Abstract**

The use of hydrochloric acid in the treatment of the bottomhole formation zone leads to the significant corrosion of metals, as well as hydrogen and chloride stress cracking of pump compressor pipes. In order to solve this problem, corrosion inhibitors are added to a hydrochloric acid solution. This article presents the results of a study of the anticorrosive activity of a number of derivatives of the class of 3-alkyl-5-amino-1H-1,2,4-triazole under the conditions of hydrochloric acid corrosion of low-carbon steel.

During the study, selected 3-alkyl-5-amino-1H-1,2,4-triazoles were synthesized. Their structure was confirmed and proved using NMR spectroscopy and HPLC/MS spectrometry. Regularities of the anticorrosive action of the investigated compounds have been established using polarization electrochemical studies and gravimetric direct corrosion tests. Corrosion rates, inhibition coefficients and degrees of protection have been calculated for all inhibitors. The probable mechanism of the inhibitory action of the studied compounds has been substantiated using quantum chemical calculations based on the density functional theory using the Gaussian program.

It was shown that the structure of the alkyl substituents has the greatest effect on the inhibitory activity of the studied compounds. The mechanism was proposed for the adsorption of the inhibitor, which explained the increase in protective properties with an increase in the length of the alkyl substituent. The high hydrophobicity of the aliphatic fragment, not involved in the chemisorption process, additionally prevents the acid solution from contacting the metal surface, while the heterocyclic moiety ensures the sorption of the inhibitor on the metal surface.

As a result, it was shown that derivatives of the homologous series of 3-alkyl-5-aminotriazole are suitable as inhibitors of acid corrosion of ST-3 steel. The minimum length of a hydrocarbon radical at which significant inhibitory activity was observed is 7 carbon atoms. Protection degrees of 65–85% were achieved when 3-heptyl-5-amino-1H-1,2,4-triazole additives at a concentration of at least 2 g/L were added to the hydrochloric acid solution.

**Keywords:** Metal corrosion, Steel, corrosion inhibitors, Heterocyclic compounds, Aminotriazoles, Physicochemical research methods, Drilling equipment

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## 1. Introduction

The intensification of production in oil fields is currently one of the priority areas for the development of the oil industry. At the same time, a large share of carbonate reservoirs in oil and gas reserves, relatively low production and low oil recovery in such oil fields make this group of reservoirs especially promising in terms of the use of new technologies for intensifying production. There are a large number of methods for influencing the bottomhole zone of wells in carbonate reservoirs. Hydrochloric acid technologies and their modifications are widespread in oil fields; they play a huge role in intensifying oil production. Their use is so high that, according to the total effect of additional oil produced from the deposit, they are equated with methods of enhanced oil recovery.

The use of hydrochloric acid in the treatment of the bottomhole formation zone leads to significant corrosion of metals, as well as hydrogen and chloride stress cracking of pump compressor pipes. As a result of corrosion, pipelines quickly become unusable, and this affects the economic effect of acid treatments. In order to solve this problem, corrosion inhibitors are added to the hydrochloric acid solution.

Various organic and inorganic compounds are used as such additives. However, many currently known corrosion inhibitors are non-biodegradable, contributing to a significant pollution of waste water and soil, and therefore, recently, research into the search for and synthesis of environmentally friendly and harmless compounds of natural origin, promising as anti-corrosion agents, are being intensified [1–2].

To date, a wide range of heterocyclic compounds exhibiting anticorrosive properties for steel have been studied. These compounds include, for example, aminopyrazoles [3], aminopyridines [4], pyrimidines [5–6], thiazoles [7], benzimidazoles [8–9], etc., however, various triazole derivatives are undoubtedly and undeniable leaders. In particular, the effect of benzotriazole (BTA) on ferrous and non-ferrous metals has been studied in detail [10–12]. This substance is a fairly versatile inhibitor for various environments. However, the BTA has some drawbacks: the indicators of degree of protection and the

coefficients of inhibition of acid corrosion of steel are very low. It is also known that it is moderately hepatotoxic, is a mutagen, and the semi-lethal dose is ~560 mg/kg [13].

Fatty acids, which are mostly environmentally friendly, biodegradable compounds involved in the metabolism of many organisms, can be used for the production of various organic compounds, including corrosion inhibitors for both ferrous and non-ferrous metals. For example, fatty acid hydrazides and thiosemicarbazides [14] and Schiff bases of fatty acids of soybean oil [15] inhibit steel corrosion. Heterocyclic corrosion inhibitors for steel based on carboxylic acids, such as imidazoles [16] and 3-alkyl-5-mercapto-1,2,4-triazoles [17] are known. At the same time, it is known that the simplest representative of the class of aminotriazoles, amitrol, possesses low toxicity ( $LD_{50}=1100$  mg/kg) [18].

Therefore, the synthesis of heterocyclic inhibitors of the class of 5-amino-3-alkyl-1,2,4-triazoles based on carboxylic acids for the investigation of their anti-corrosion properties under the conditions of acid corrosion of steel is an important and urgent task. The goal of this study was the investigation of anti-corrosion activity of derivatives of the class of 3-alkyl-5-amino-1H-1,2,4-triazole under the conditions of hydrochloric acid corrosion of low-carbon steel.

## 2. Experimental

### 2.1. Synthesis of starting compounds

General procedure for the synthesis of 3-alkyl-5-amino-1H-1,2,4-triazoles.

The corresponding carboxylic acid was added in portions with stirring to a mixture of 100 ml of toluene with aminoguanidine carbonate (0.2 M), 0.21 M. The mixture was carefully heated to 50–70°C and, after the evolution of carbon dioxide had ceased, it was boiled with a Dean-Stark apparatus and a reflux condenser. After the separation of water in the trap ceased, the reaction mass was cooled and the solvent was decanted. The residue was ground and washed on the filter with toluene, dried, and recrystallized from a boiling mixture of isopropyl alcohol and petroleum ether. The precipitate formed after cooling was filtered, washed with petroleum ether, and dried at 60°C.

*3-methyl-5-amino-1H-1,2,4-triazole (b)*. Yield 65–70%, mp 148–150 °C. White powder. <sup>1</sup>H NMR spectrum: 2.02 (s, 3H, CH<sub>3</sub>); 5.73 (s, 2H, NH<sub>2</sub>); 11.50 (s, H, NH). Determined, m/z: 99.0672 [M+H]<sup>+</sup>. C<sub>3</sub>H<sub>6</sub>N<sub>4</sub>+H<sup>+</sup>. Calculated, m/z: 99.0665.

*3-ethyl-5-amino-1H-1,2,4-triazole (c)*. Yield 57–63%, mp 139–141 °C. White powder. <sup>1</sup>H NMR spectrum: 1.02 (t, 3H, J=7.5, CH<sub>3</sub>); 2.40 (q, J=7.5, 2H, CH<sub>2</sub>); 5.70 (s, 2H, NH<sub>2</sub>); 11.49 (s, H, NH). Determined, m/z: 113.0816 [M+H]<sup>+</sup>. C<sub>4</sub>H<sub>8</sub>N<sub>4</sub>+H<sup>+</sup>. Calculated, m/z: 113.0822.

*3-butyl-5-amino-1H-1,2,4-triazole (d)*. Yield 55–57%, mp 124–126 °C. White powder. <sup>1</sup>H NMR spectrum: 0.87 (t, J=7.5, 3H, CH<sub>3</sub>); 1.29–1.37 (m, 2H, CH<sub>2</sub>); 1.44–1.51 (m, 2H, CH<sub>2</sub>); 2.38 (t, J=7.3, 2H, CH<sub>2</sub>); 5.61 (s, 2H, NH<sub>2</sub>); 11.49 (s, H, NH). Determined, m/z: 141.1127 [M+H]<sup>+</sup>. C<sub>6</sub>H<sub>12</sub>N<sub>4</sub>+H<sup>+</sup>. Calculated, m/z: 141.1135.

*3-pentyl-5-amino-1H-1,2,4-triazole (e)*. Yield 55–64%, mp 124–127 °C. White powder. <sup>1</sup>H NMR spectrum: 0.86 (t, J=7.5, 3H, CH<sub>3</sub>); 1.29–1.38 (m, 4H, 2CH<sub>2</sub>); 1.52–1.59 (m, 2H, CH<sub>2</sub>); 2.38 (t, J=7.3, 2H, CH<sub>2</sub>); 5.56 (s, 2H, NH<sub>2</sub>); 11.49 (s, H, NH). Determined, m/z: 155.1299 [M+H]<sup>+</sup>. C<sub>7</sub>H<sub>14</sub>N<sub>4</sub>+H<sup>+</sup>. Calculated, m/z: 155.1292.

*3-heptyl-5-amino-1H-1,2,4-triazole (f)*. Yield 60–64%, mp 120–124 °C. White powder. <sup>1</sup>H NMR spectrum: 0.85 (t, J=7.5, 3H, CH<sub>3</sub>); 1.25–1.36 (m, 8H, 4CH<sub>2</sub>); 1.52–1.59 (m, 2H, CH<sub>2</sub>); 2.38 (t, J=7.3, 2H, CH<sub>2</sub>); 5.55 (s, 2H, NH<sub>2</sub>); 11.49 (s, H, NH). Determined, m/z: 183.1301 [M+H]<sup>+</sup>. C<sub>9</sub>H<sub>18</sub>N<sub>4</sub>+H<sup>+</sup>. Calculated, m/z: 183.1605.

## 2.2. Methods for structure proof of compounds

Control of the individuality of the reagents and the obtained compounds and the course of the reaction, was carried out using thin layer chromatography (hereinafter referred to as TLC) on Silufol UV-254 plates. Chloroform was used as the eluent; the development of chromatograms was carried out in UV light and iodine vapour. <sup>1</sup>H NMR spectra were recorded using a Bruker AC-300 (operating frequency 300 MHz) in pulsed Fourier mode in a DMSO-d<sub>6</sub>; The assignment of the signals was carried in relation to the residual signals of the proton of the deuterium solvent. Mass spectra were recorded using an MX-1321 spectrometer with direct injection of the sample into the ion source at 100–150 °C and an accelerating voltage of 70

eV. The melting point was determined using a PTP-M device.

## 2.3. Electrochemical research

Polarization curves were obtained on an electrode made of ST-3 steel (with an area of 1.0 cm<sup>2</sup>) in an electrochemical cell with undivided electrode spaces using an IPC-PRO potentiostat. The working electrode was preliminarily cleaned with K2000 sandpaper and degreased with ethyl alcohol. Electrode potentials (*E*) was measured relative to the silver chloride electrode, connecting the space of the electrochemical cell and the reference electrode through an electrolytic bridge based on agar-agar and sodium nitrate, and recalculated to the scale of a standard hydrogen electrode (potential was +202 mV relative to SHE). A platinum grid was used as an auxiliary electrode.

The test substances were introduced into the acid until the required concentration was obtained. The electrodes were placed in the prepared solution and kept until the onset of a stationary state for 30 min. After the open-circuit potential (*E*<sub>cor</sub>) was established, polarization curves with a potential scan rate of 0.2 mV/s in the anode and cathode directions were obtained. Polarization curves were recorded until the current density reached 0.1 A cm<sup>-2</sup>.

## 2.4. Calculation of the corrosion rate using the polarization resistance method

The rate of corrosion in current units was determined by the polarisation resistance technique as summarized by Mansfeld [19].

The studies were carried out using a three-electrode cell with undivided cathode and anode spaces without mixing under natural aeration conditions, the reference electrode was silver chloride (potential +202 mV relative to SHE), and the auxiliary electrode was a platinum grid. The reference electrode was separated from the cell by an electrolytic bridge based on agar-agar and NaNO<sub>3</sub>.

The working electrode was preliminarily cleaned with P2000 sandpaper, degreased with ethyl alcohol (96%), and washed with distilled water. The electrodes were placed in the prepared solution and kept until the onset of a stationary state for 30 min. When the steady state was

reached, the electrode was polarized in the range of  $\pm 30$  mV from the value  $E_{\text{cor}}$  in potentiodynamic mode with a scanning rate of 0.2 mV/s.

Polarization resistance  $R_p$  was determined as the slope of the polarization curve at the point  $E_{\text{cor}}$  in the coordinates  $\Delta E - i$ , where  $\Delta E$  is the difference between the current electrode potential and the open-circuit potential ( $E - E_{\text{cor}}$ ). Next, the dependence was plotted with the coordinates  $2.3 \cdot R_p \cdot i - \Delta E$ . Coefficients  $b_a$  and  $b_c$  (Tafel slopes of the cathode and anode segments of the polarization curve) were determined using the TableCurve 2D program as the approximation parameters of the equation:

$$2.3 \cdot R_p \cdot I = \frac{b_a \cdot b_c}{b_a + b_c} \left[ \exp\left(\frac{E - E_{\text{cor}}}{b_{1a}}\right) - \exp\left(-\frac{E - E_{\text{cor}}}{b_{2c}}\right) \right] \quad (1)$$

The corrosion current was calculated taking into account the obtained coefficients according to the equation:

$$I_{\text{cor}} = \frac{B}{R_p} \quad (2)$$

For the comparison of the data obtained in various studies, the values of the corrosion current density ( $i_{\text{cor}}$ ) calculated using the expression will be presented further:

$$i_{\text{cor}} = \frac{I_{\text{cor}}}{S}, \quad (3)$$

where  $S$  is the geometric area of the electrode. For the convenience of further comparison of the obtained data, the ratio of the corrosion current density of each test sample to the current density of the background experiment was calculated ( $i_{\text{cor}}^0 \approx 6.8$  mA/cm<sup>2</sup>):

$$i_{\text{cor(relative)}} = \frac{i_{\text{cor}}}{i_{\text{cor}}^0} \times 100\%. \quad (4)$$

Measurements for each concentration of the substance were made at least 5 times until reproducible data were obtained with subsequent statistical processing of the measurement results.

### 2.5. Gravimetric direct corrosion tests

Corrosion tests were carried out on steel plates (20×40 mm, thickness 1.2 mm). Each sample was preliminarily polished with K 1000 fine-grained sandpaper, after which it was washed

with distilled water, ethanol, and dried with filter paper. The experiments were carried out in a 24% HCl solution (for 7 days) under natural aeration without stirring for three samples in parallel (for each inhibitor concentration). After testing, the plates were washed with distilled water and treated with compositions in accordance with GOST 9.907-83.

The corrosion rate was determined according to the weight loss of the samples and was calculated using the formula:

$$k_{\text{inh}} = \frac{\Delta m}{S \cdot t} \quad (5)$$

where  $\Delta m = m_0 - m$  ( $m_0$  is the weight of the sample before the start of the experiment,  $m$  is the weight of the sample after test, g),  $S$  is the total surface area of the plate, m<sup>2</sup>.

For each solution, the corrosion rate  $k_0$  without inhibitor additive was determined ( $k_{0(\text{medium})} \approx 16.9 \pm 0.5$  g/m<sup>2</sup> day is the average value of the corrosion rate without the addition of an inhibitor, obtained over the course of the studies). The effectiveness of the inhibitory action of aminotriazole derivatives was evaluated according to the value of the inhibition coefficient:

$$\gamma = \frac{k_0}{k_{\text{inh}}} \quad (6)$$

and the degree of protection:

$$Z = \left[ \frac{k_0 - k_{\text{inh}}}{k_0} \right] \cdot 100\%, \quad (7)$$

where  $k_0$  and  $k_{\text{inh}}$  are the corrosion rates in the background solution and in the solution with the inhibitor, respectively.

### 2.6. Quantum-chemical calculations

All molecules of the synthesized compounds were fully optimized using the density functional theory (DFT) with the B3LYP functional using the 6-31G (d, p) basis in the Gaussian program [20]. The optimized geometry shows non-negative frequencies, resulting in the molecules being positioned at minimum energy on the potential energy surface. Determination of the energies of HOMO and LUMO molecular orbitals, their difference HLG (HOMO-LUMO-gap), as well as the ionization potential ( $IP$ ), electron affinity ( $EA$ ), electronegativity ( $\chi$ ), absolute hardness ( $\eta$ ),

and absolute softness ( $\sigma$ ) for all molecules were carried out at the same level of theory.

According to the density functional theory, the absolute hardness ( $\eta$ ) is defined as [21]

$$\eta = \frac{1}{2} \frac{\partial \mu}{\partial N} = \frac{1}{2} \frac{\partial^2 E}{\partial N^2}, \quad (8)$$

where  $\mu$  is the chemical potential,  $N$  is the number of electrons, and  $E$  – energy. R. G. Pearson proposed a working definition of absolute hardness as

$$\eta = \frac{IP - EA}{2}, \quad (9)$$

where  $IP$  and  $EA$  are ionization potential and electron affinity. Also, according to Koopmans' theorem  $IP$  and  $EA$  are defined as

$$IP = -E_{\text{HOMO}}; \quad EA = -E_{\text{LUMO}}, \quad (10)$$

$E_{\text{HOMO}}$  and  $E_{\text{LUMO}}$  are the energies of the highest occupied and lowest unoccupied molecular orbitals.

Electronegativity ( $\chi$ ) is also defined in terms of HOMO and LUMO energies as

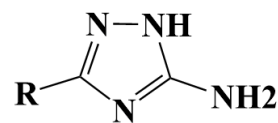
$$\chi = \frac{IP + EA}{2}. \quad (11)$$

According to formulas described above (9, 11), the hardness is a measure of the resistance to changes in the electron cloud of a chemical system and is an important parameter in the reaction chemistry. Absolute softness ( $\sigma$ ) is inversely proportional to hardness. It is generally accepted [21] that in the homologous series of organic compounds, the most reactive substances have a higher softness value in comparison with their homologues. This idea makes possible the theoretical evaluation and comparison of the degree of binding of inhibitors of the same class of organic compounds with metal and, as a result, estimate their probable inhibitory ability.

### 3. Results and discussion

Along with the inhibitors synthesized in the study (Fig. 1), Amitrol, a commercially available 3H-5-amino-1H-1,2,4-triazole **a**, was also studied in corrosion tests. Solutions with inhibitor concentrations of 1 g/l and 2 g/l were studied.

As a result of potentiodynamic studies, it was found that the addition of 3-H-5-amino-



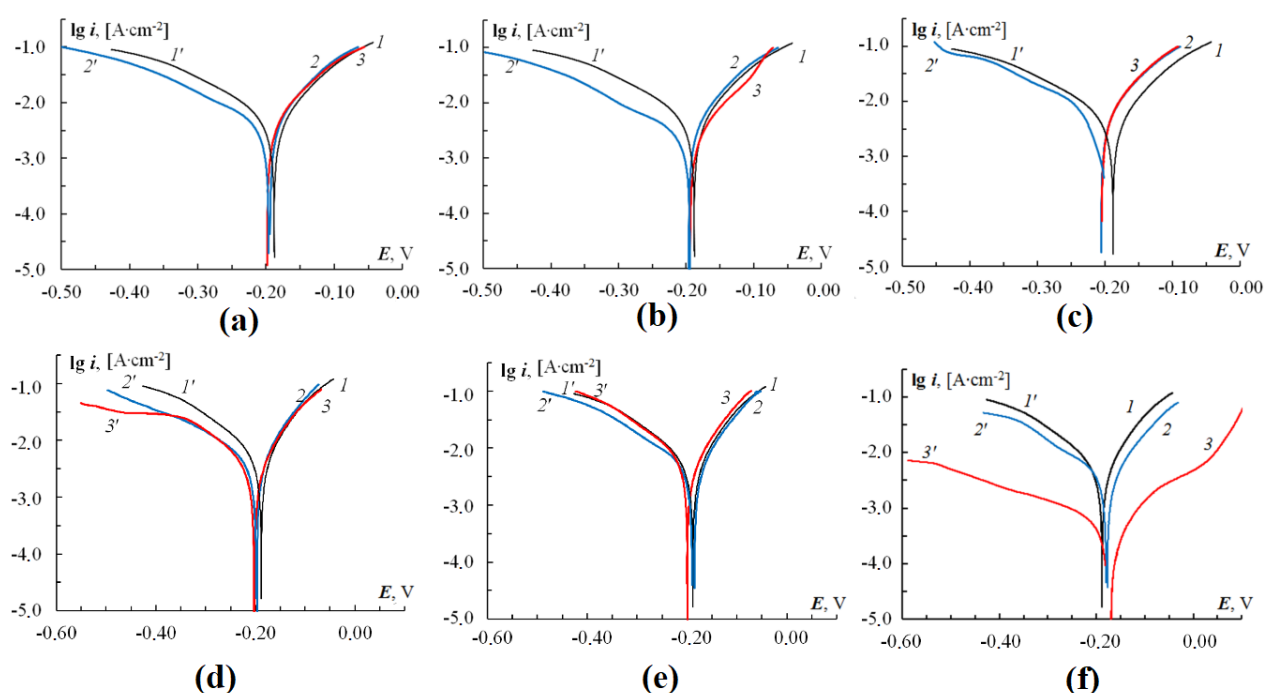
**R:** H (**a**), CH<sub>3</sub> (**b**), C<sub>2</sub>H<sub>5</sub> (**c**),  
C<sub>4</sub>H<sub>9</sub> (**d**), C<sub>5</sub>H<sub>11</sub> (**e**), C<sub>7</sub>H<sub>15</sub> (**f**)

**Fig. 1.** Structure of the studied derivatives of 1,2,4-triazole

1H-1,2,4-triazole **a** to the acid solution up to 2 g/l slightly changed the shape and position of the anodic and cathodic parts of the polarization curves. (Fig. 2). However, for the cathode sections, insignificant decrease in the current density at all studied concentrations of the inhibitor ( $C_{\text{inh}}$ ) was revealed. The addition of 3-methyl-5-amino-1H-1,2,4-triazole up to 2 g/l had a similar effect on the nature of the polarization curves. Thus, for 3-methyl- and 3H-5-amino-1H-1,2,4-triazoles, we can assume an insignificant inhibitory effect due to inhibition of the cathodic reduction half-reaction of the oxidizer.

The addition of 3-ethyl-5-amino-1H-1,2,4-triazole to the acid solution up to 2 g/l slightly changed the shape and position of the anodic and cathodic segments of the polarization curves relative to the control measurement without amino-1H-1,2,4-triazole. The nature of the polarization curves for 3-butyl-5-amino-1H-1,2,4-triazole and 3-pentyl-5-amino-1H-1,2,4-triazole was similar to the results for 3-ethyl derivatives. Thus, the presence of an inhibitory effect according to potentiodynamic measurements for compounds **b-e** is unlikely.

With the addition of 3-heptyl-5-amino-1H-1,2,4-triazole at a concentration of 1 g/L, the polarization curves were hardly distinguishable from the control curves; only a slight decrease in current densities was observed in all parts of the curve. With an increase in concentration to 2 g/l, a significant, up to 1 order of magnitude, decrease in the density of the anode and cathode current was observed at a given value of the electrode potential. At the same time, the open-circuit potential was slightly different from the control value. Such a course of the polarization curve



**Fig. 2.** Anodic ( $I$ - $3$ ) and cathodic ( $I'$ - $4'$ ) polarization curves of ST-3 steel in HCl (24 %) at  $C_{inh}$  (g/L):  $1, I'$  – 0.0;  $2, 2'$  – 1.0;  $3, 3'$  – 2.0, obtained by the addition of 3-*H*-5-amino-1*H*-1,2,4-triazole (a), 3-methyl-5-amino-1*H*-1,2,4-triazole (b), 3-ethyl-5-amino-1*H*-1,2,4-triazole (c), 3-butyl-5-amino-1*H*-1,2,4-triazole (d), 3-pentyl-5-amino-1*H*-1,2,4-triazole (e), 3-heptyl-5-amino-1*H*-1,2,4-triazole (f)

indicates the presence of a noticeable inhibitory effect of 3-heptyl-5-amino-1*H*-1,2,4-triazole in relation to steel in concentrated hydrochloric acid.

The results of direct corrosion tests in general correlated with electrochemical studies. Degrees of protection  $Z$  for compounds a-e did not exceed 10-15%, which for the direct tests can

be considered as evidence of the absence of an inhibitory effect. The introduction of 3-heptyl-5-amino-1*H*-1,2,4-triazole f into a hydrochloric acid solution significantly reduced the corrosion of the studied steel plates (protection degree  $Z \sim 65\%$  at an inhibitor concentration of 2 g/l). Calculations carried out using the polarization resistance method also confirmed this trend

**Table 1.** Corrosion rate and degree of protection data calculated by polarization resistance method and direct corrosion tests

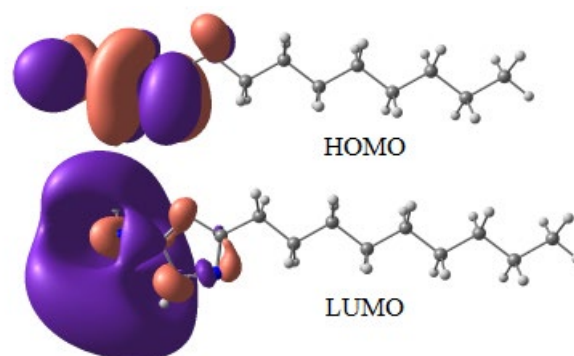
No.	Inhibitor	$C_{inh}$ , g/l	$C_{inh}$ , g/l	$\gamma$	$Z$ , %	$I_{cor}^{(abs)}$ , mA/cm <sup>2</sup>	$i_{cor}^{(rel)}$
a	5-amino-1 <i>H</i> -1,2,4-triazole	1.00	14.19	1.19	16.04	6.2±0.9	8.8 %
		2.00	14.19	1.19	16.04	6.8±0.9	0.0 %
b	3-methyl-5-amino-1 <i>H</i> -1,2,4-triazole	1.00	15.41	1.10	8.82	6.8±0.7	0.0 %
		2.00	15.20	1.11	10.06	6.6±0.6	2.9 %
c	3-ethyl-5-amino-1 <i>H</i> -1,2,4-triazole	1.00	13.93	1.21	17.57	7.6±1.2	-11.7 %
		2.00	13.87	1.22	17.93	9.8±0.8	-44.1 %
d	3-butyl-5-amino-1 <i>H</i> -1,2,4-triazole	1.00	12.37	1.37	26.80	7.7±0.9	-13.2 %
		2.00	12.28	1.38	27.34	6.3±1.3	7.3 %
e	3-pentyl-5-amino-1 <i>H</i> -1,2,4-triazole	1.00	14.55	1.16	13.91	8.5±0.1	-24.9 %
		2.00	13.24	1.28	21.66	8.6±0.8	-26.5 %
f	3-heptyl-5-amino-1 <i>H</i> -1,2,4-triazole	1.00	9.86	1.71	41.66	7.1±0.7	-4.4 %
		2.00	5.74	2.94	66.04	0.8±0.5	89.0 %

(Table 1). With an inhibitor concentration of 2 g/l, the average degree of protection for the heptyl derivative **f** was ~90%. For all other compounds, the degrees of protection calculated as a result of electrochemical studies indicate the absence of an inhibitory effect or the intensification of the course of electrode processes in their presence (at  $i_{cor}(\text{rel}) < 0$ )

The analysis of the results of quantum chemical calculations for the molecules of studied corrosion inhibitors (Table 2) demonstrated the absence of significant change of the orbital characteristics with an increase in the length of the aliphatic fragment. The main electron density is distributed over the molecular orbitals of the heterocyclic fragment and the exocyclic amino group of the inhibitors. This finding shows that the heterocyclic matrix, as well as the amino group with high probability are the main centre of triazole molecules involved in adsorption and binding to the metal surface (Fig. 3). Thus, correlating the results of corrosion tests and quantum chemical calculations, we can conclude

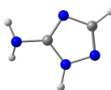
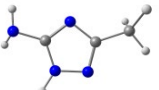
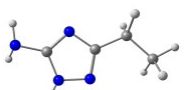
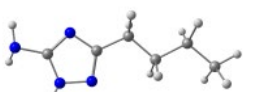
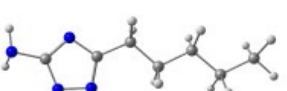
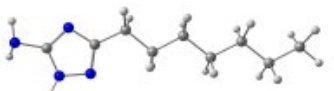
that the structure of the alkyl substituent, and not the electronic structure of the molecule as a whole, has the greatest effect on the inhibitory activity of the studied compounds, since the distribution of electron densities in the molecules of inhibitors practically does not change with changes in the structure of the side aliphatic substituent.

As can be seen from the test results, effective protection of steel from acid corrosion in



**Fig. 3.** HOMO and LUMO visualization of the 3-heptyl-5-amino-1H-1,2,4-triazole molecule

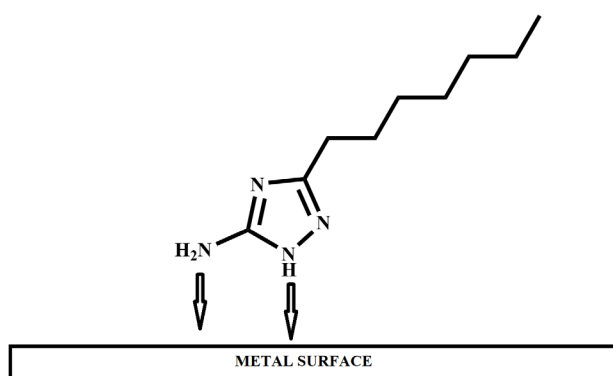
**Table 2.** Optimized structures, calculated HOMO, LUMO energies, HOMO-LUMO gap (HLG), Ionization Potential ( $IP$ ), Electron Affinity ( $EA$ ), Electronegativity ( $\chi$ ), Absolute Hardness ( $\eta$ ) and Softness ( $\sigma$ ) in eV at B3LYP/6-311+G (d,p) level of theory

No.	Structure	HOMO	LUMO	HLG	$IP$	$EA$	$\chi$	$\eta$	$\sigma$
<b>a</b>		-6.62	-0.54	6.08	6.62	0.54	3.58	3.04	0.33
<b>b</b>		-6.43	-0.50	5.93	6.43	0.50	3.46	2.96	0.34
<b>c</b>		-6.42	-0.49	5.93	6.42	0.49	3.46	2.96	0.34
<b>e</b>		-6.41	-0.50	5.91	6.41	0.50	3.46	2.96	0.34
<b>e</b>		-6.41	-0.50	5.91	6.41	0.50	3.46	2.96	0.34
<b>f</b>		-6.41	-0.50	5.91	6.41	0.50	3.46	2.95	0.34

hydrochloric acid is possible by increasing the length of the aliphatic substituent in the homologous series of 3-alkyl-5-amino-1H-triazoles to 7 carbon atoms.

This feature of steel passivation can be explained by an increase in the lyophilic nature of the inhibitor molecule. Probably, the introduction of hydrophobic substituents into the cycle reduces the interaction of the organic molecule with the solvent and increases its adsorption capacity.

As a result, most probably the formation of protective triazole layers on the metal surface occurs under the considered conditions. (Fig. 4). Probably, a self-organization mechanism occurs, in which the inhibitor molecule is oriented on the metal surface according to the “head-tail” principle, when the heterocyclic moiety provides self-organization and binding of the inhibitor to the metal surface, and the lateral hydrophobic aliphatic substituent of the molecule prevents contact of the acid solution with a metal surface. This mechanism explains the increase in the protective properties of inhibitors with an increase in the length, and, consequently, in the hydrophobic properties of the alkyl substituent.



**Fig. 4.** Schematic diagram of the formation of protective layers by the example of 3-heptyl-5-amino-1H-1,2,4-triazole

Earlier in the study [22], the mechanism of formation of such layers was also studied in detail for copper chloride corrosion. It was shown that when copper was protected with 3-alkyl-5-aminotriazoles, inhibitory activity was observed already when 3-butyl-1H-5-aminotriazole was introduced into the system at concentrations of at least 0.001 M.

The results obtained in this study do not contradict the results of earlier studies, as well as literature data.

Thus, it was found that inhibitory activity under the condition of hydrochloric acid corrosion of steel is probable for compounds of the homologous series of 3-alkyl-5-aminotriazole. The minimum length of the hydrocarbon fragment, at which a significant protective effect is observed, is 7 carbon atoms.

#### 4. Conclusions

The study performed using polarization methods and direct corrosion tests allowed establishing that derivatives of the homologous series of 3-alkyl-5-aminotriazole are suitable as inhibitors of chloride acid corrosion on ST-3 steel.

The minimum length of the hydrocarbon radical, at which significant anti-corrosion properties are observed, is 7 carbon atoms. In this case, the minimum concentration of inhibition is 1 g/L. However, high degrees of protection of 65–85% are achieved when 3-heptyl-5-amino-1H-1,2,4-triazole is added to the hydrochloric acid solution at a concentration of at least 2 g/l.

#### Author contributions

All authors made an equivalent contribution to the preparation of the publication.

#### Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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