Copper corrosion inhibition in chloride environments by 3-(*N*-hetaryl)-5-amino-1*H*-1,2,4-triazoles

O.A. Kozaderov,[1] **Kh.S. Shikhaliev,**[1]*** Ch. Prabhakar,**[2]*** D.S. Shevtsov,**[1] **A.A. Kruzhilin,**[1] **E.S. Komarova,**[1] **A.Yu. Potapov**[1] **and I.D. Zartsyn**[1]

[1]*Voronezh State University, Universitetskaya pl. 1, Voronezh, 394018, Russian Federation*
[2]*National Institute of Technology Kurukshetra, Kurukshetra, 136119, India*
*E-mail: shikh1961@yandex.ru, chetti@nitkkr.ac.in

Abstract

According to the results of experimental electrochemical measurements and corrosion tests, the effectiveness of inhibiting copper corrosion in chloride media by *N*-hetaryl derivatives of 5-amino-1*H*-1,2,4-triazole was evaluated. It was found that addition of any of the organic additives studied into a borate buffer solution in the presence of 10 mM NaCl leads to a significant ennoblement of the pitting potential of copper electrode. At the same time, the anodic and cathodic processes on copper in the presence of 3-(4-methylpiperazin-2-yl)-5-amino-1*H*-1,2,4-triazole at a concentration of 0.1–1.0 mM generally proceed at a higher rate than in the absence of an organic additive. On the contrary, addition of 3-(piperidin-1-yl)-, 3-(4-phenylpiperazin-2-yl)- and 3-(4-benzylpiperazin-1-yl)-5-amino-1*H*-1,2,4-triazoles to the solution decreases the rate of both the cathodic process and anodic oxidation of copper, regardless of the nature of an inhibiting additive and its concentration. In addition, in the presence of these inhibitors, the current density of copper electrode passivation decreases markedly. All the compounds studied are characterized by moderate degrees of copper protection in neutral chloride media (at least 56%). The degree of protection against acid corrosion for all the inhibitors studied is 30–60% and increases with increasing concentration of an organic additive. The greatest protective effect is provided by 3-(piperidin-1-yl)-5-amino-1*H*-1,2,4-triazole in neutral or acidic chloride solutions. None of the inhibitors proved to be highly effective against atmospheric corrosion of copper: the first corrosion damage appears within 40–60 hours. Using DFT simulations, a correlation was found between the inhibitory effect and the molecular structure of the 5-amino-1*H*-1,2,4-triazole derivatives studied.

Key words: copper, corrosion, chloride, 5-amino-1H-1,2,4-triazoles.

Introduction

Copper is one of the most important nonferrous metals used in industry and in water distribution networks due to its high thermal and electrical conductivity and impressive mechanical workability. The copper potential is relatively noble, however its corrosion rate is rather significant in sea water and other environments containing different corrosive

species like chloride, sulphate and nitrate ions, which can induce dangerous pitting corrosion [1−6]. The anodic dissolution of copper in chloride environments is generally accepted to be influenced by the chloride ions concentration C_{Cl^-}, and at $C_{Cl^-} < 1$ M the process occurs through the formation of non-protective CuCl, which is converted to soluble $CuCl_2$ by reacting with excess chloride [6]. Copper can only be passivated in neutral, weakly acidic or alkaline solutions by forming an oxide surface layer [7]. Besides, inhibition of the corrosion process with special organic compounds is an effective way to protect copper materials in various media.

Azoles and their derivatives are considered to be the most effective organic inhibitors against copper corrosion [8−17]. The inhibiting properties of azoles are provided by the presence of H atoms bound to the N atom in the azole cycle of the molecule, which makes azoles relatively strong acids capable of forming salts with metal ions. As a consequence, these nitrogen-based heterocyclic compounds can be coordinated with Cu, Cu^+ or Cu^{2+} *via* the lone electron pairs of their N atoms to form complexes with copper [18−21]. 1,2,3-Benzotriazole and its derivatives have been studied most deeply and used most widely, and their indisputable advantage is the ability to protect copper not only in neutral environments, including humid atmospheres, but also in solutions of corrosive acids [10−14, 17]. Along with benzotriazole derivatives, more hydrophilic 1,2,4-triazole derivatives are also attractive, as they can act as effective corrosion inhibitors for copper in chloride environments because of the unique structural property of the triazole moiety [22, 23]. Some amino-1,2,4-triazoles can be even more effective than 1,2,3-benzotriazole as copper corrosion inhibitors in neutral aqueous solutions [10, 13, 24, 25]. For instance, 3-amino-1,2,4-triazole has rather a high efficiency in the inhibition of copper corrosion, and in spite of its low hydrophobicity, it can be strongly adsorbed on the metal surface to form a complex with Cu, which more effectively prevents the formation of soluble copper chloride complexes [10, 24, 26, 27] and pitting formation on copper surface in borate buffer solution containing chlorides or sulphates [28].

It is assumed that the first step in the inhibition mechanism involves the adsorption of an inhibitor onto the copper metal surface. It was shown [13, 29] that introduction of hydrophobic substituents into the 3-amino-1,2,4-triazole molecule significantly increases the adsorption efficiency of the inhibitor on copper surface, while hydrophobization does not lead to a significant decrease in solubility in water. In this work, we study the copper corrosion inhibition effect in chloride environments provided by new *N*-hetaryl derivatives of 5-amino-1*H*-1,2,4-triazole characterized by the presence of hydrophobic substituents and a satisfactory level of water solubility. Along with the corrosion tests in an acidic chloride environment and in a corrosive humid chloride-containing atmosphere, electrochemical measurements were carried out in a borate buffer in the presence of 10 mM NaCl as an activating additive. This makes it possible to obtain information on the passivating effect of triazoles and their ability to stabilize the passive state of copper under conditions of competitive adsorption of the organic inhibitor and chloride. To establish a correlation between the experimental data on the inhibition effect of 5-amino-1*H*-1,2,4-
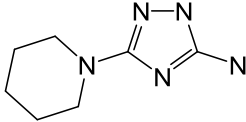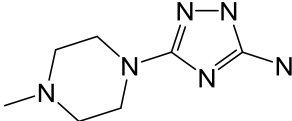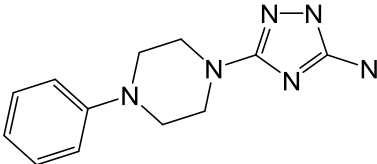
triazoles and their molecular structure, the method of quantum-chemical DFT simulations was used [23, 30].
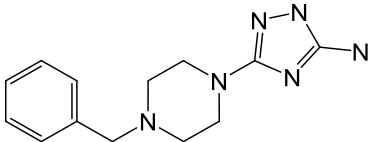
The purpose of this work is to experimentally evaluate the effectiveness of copper corrosion inhibition in chloride media by *N*-hetaryl derivatives of 5-amino-1*H*-1,2,4-triazole based on electrochemical studies and corrosion tests, as well as to establish the role of the chemical structure of the inhibitors in the formation of their protective properties using DFT simulations.

Experimental

Electrochemical measurements were carried out at room temperature (~25°C) on M1 copper electrodes in a non-stirred borate buffer aqueous solution (pH 7.4) under natural aeration conditions in the presence of an inhibitor and an activating additive (10 mM sodium chloride) in a three-electrode electrochemical cell with non-separated electrode spaces (to improve the performance of non-stationary measurements). 5-Amino-1*H*-1,2,4-triazole derivatives synthesized in Voronezh State University were used as inhibitors. Their names and structural formulas are given in Table 1. A saturated silver chloride reference electrode was placed in a separate vessel connected to the electrochemical cell *via* a salt bridge filled with a saturated solution of potassium nitrate. A platinum grid was used as the auxiliary electrode. The working copper electrode was preliminarily cleaned on emery paper K3000, degreased with ethyl alcohol (96%) and washed with distilled water. The potentials of the working electrode (E) are given in the standard hydrogen electrode (SHE) scale. The current density i was calculated by dividing the current I by the geometric area of the working electrode (0.75 cm^2).

Table 1. Inhibitor names, structures and solubility in water.

Symbol	Name	Formula	Solubility
A	3-(piperidin-1-yl)-5-amino-1*H*-1,2,4-triazole		
B	3-(4-methylpiperazin-2-yl)-5-amino-1*H*-1,2,4-triazole		>10 mM
C	3-(4-phenylpiperazin-2-yl)-5-amino-1*H*-1,2,4-triazole		

Symbol	Name	Formula	Solubility
D	3-(4-benzylpiperazin-1-yl)-5-amino-1*H*-1,2,4-triazole		> 5 mM

Electrochemical measurements were performed using an IPC-PRO potentiostat. To remove the oxide film formed in air, the working Cu electrode was cathodically pre-polarized at $E = -0.60$ V for 15 min, after which the polarization was turned off and the electrode was kept in the solution until a steady free corrosion potential (E_{corr}) was established (within 3–5 min).

Then a NaCl solution was introduced into the working solution with stirring, providing the concentration of chloride ions $C_{Cl^-} = 10$ mM, as well as the inhibitors under study at a concentration of $C_{inh} = 0.01$, 0.10 and 1.00 mM. After stabilization of a new value of E_{corr}, the polarization curve was recorded by scanning the potential in the anodic or cathodic direction at a scan rate of 0.2 mV/s. The pitting potential (E_{pit}) was determined by a sharp increase in current on the anodic polarization curve with subsequent visual identification of the pitting on the electrode surface. The error in measuring E_{pit} did not exceed 0.005 V. The corrosion current density (i_{corr}) was determined by the Mansfeld method of polarization resistance [31, 32]. A polarization curve was preliminarily recorded by scanning the potential from $E = E_{corr} - 0.03$ V to $E = E_{corr} + 0.03$ V at a scan rate of 0.2 mV/s. Then, the polarization resistance R_p was calculated as the tangent (at E_{corr} potential) to the polarization curve, reconstructed in ΔE, i-coordinates ($\Delta E = E - E_{corr}$). Then, the curve was reconstructed in coordinates $2.3 \cdot R_p \cdot i - \Delta E$, and using the TableCurve program, we determined the Tafel parameters of cathodic and anodic half-reactions b_a and b_c as the approximation parameters of the equation

$$2.3 \cdot R_p \cdot i = \frac{b_a \cdot b_c}{b_a + b_c} \left[\exp\left(\frac{\Delta E}{b'_{1a}} \right) - \exp\left(-\frac{\Delta E}{b'_{2c}} \right) \right] \frac{n!}{r!(n-r)!},$$

which at $\Delta E = 0$ gives the value of i_{corr}. Measurements for each inhibitor concentration were carried out at least 5 times to obtain reproducible data, which were statistically processed.

The effectiveness of the inhibitory effect of 5-amino-1*H*-1,2,4-triazole derivatives was evaluated by the degree of protection

$$Z_i = \frac{i_{corr,0} - i_{corr,inh}}{i_{corr,0}} \cdot 100\%,$$

where $i_{corr,0}$ and $i_{corr,inh}$ are the corrosion current densities in the absence and in the presence of an inhibitor, respectively.

Corrosion tests were carried out in accordance with GOST 9.905-82 "Corrosion test methods" on copper plates with an area of $S = 20 \times 50$ mm^2 and a thickness of $d = 0.2$ mm. Each sample was pre-polished with fine-grained K1000 sanding paper, then washed with distilled water, ethanol, and dried with filter paper. Experiments with a duration of $t = 7$ days were performed with three samples simultaneously in a non-stirred, naturally aerated 1% aqueous solution of HCl. After testing the plates were washed with distilled water and treated in accordance with GOST 9.907-83 "Methods for the removal of products after corrosion tests". The corrosion rate was determined by the mass loss of the samples and was calculated by the formula:

$$k = \frac{m_0 - m}{S \cdot t},$$

where m_0 and m are the sample mass before and after corrosion tests, respectively. The effectiveness of the inhibitory effect of derivatives of 5-amino-1*H*-1,2,4-triazole was evaluated by the inhibition coefficient

$$\gamma = \frac{k_0}{k_{inh}}$$

and degree of protection

$$Z_k = \frac{k_0 - k_{inh}}{k_0} \cdot 100\% ,$$

where k_0 and k_{inh} are the corrosion rates in the HCl solution in the absence and in the presence of an inhibitor, respectively. The parameter k_0 was 44 g·m^{-2}·day^{-1}. The study of anticorrosion action was performed for systems with inhibitor concentrations of 1, 5 and 10 mM.

The tests in a salt fog chamber simulated the atmospheric corrosion of copper in order to identify the inhibitory effect of 5-amino-1*H*-1,2,4-triazole derivatives for the inter-operational protection of copper. Studies were carried out on copper plates, which were previously cleaned on sandpaper of various grit, polished and degreased with acetone. The protective film of inhibitors was formed by immersion of copper plates into aqueous solutions of inhibitors for 60 minutes at a temperature of 60°C. The samples were dried and placed in a chamber, inside which a 5% aqueous solution of NaCl (pH 6.5–7.2, GOST R 52763-2007) was sprayed hourly and the air humidity was 95–100%. The samples were inspected 3 times a day to determine the time of appearance of the first corrosion damage (τ_{corr}).

Geometrical optimization of molecules of the inhibitors being studied was performed using density functional theory (DFT) using B3LYP functional with 6-311+ G (d, p) basis set in Gaussian 09 package [36]. The optimized geometry of molecules is without negative frequency and hence is at lowest energy state on the potential energy surface. Further, to calculate the lowest five electronic excitations, TDDFT calculations were performed on the

optimized geometries. The frontier molecular orbitals were used to predict the inhibition efficiency of the molecules. Within the limitation of the Koopmans theorem, the frontier orbital energies are given by the following equation [34]:

$$-E_{HOMO} = IP \text{ and } -E_{LUMO} = EA$$

where *IP* is the ionization potential and *EA* is the electron affinity. Chemical hardness (η) is calculated using the following equation [35, 36]:

$$\eta = \frac{IP - EA}{2}.$$

Softness (σ) is defined as reciprocal of hardness and is calculated as follows:

$$\sigma = \frac{1}{\eta}.$$

Results and discussion

Addition of the inhibitors being studied to the chloride solution results in a shift in the free corrosion potential of the copper electrode in the positive direction. With an increase in the concentration of the inhibitor, ennoblement of E_{corr} is more pronounced (Table 2), regardless of the structure of the *N*-hetaryl substituent. The corrosion potential shift is the smallest (no more than ~50 mV) in the case of 3-(piperidin-1-yl)- and 3-(4-methylpiperazin-2-yl)-5-amino-1*H*-1,2,4-triazoles. Addition of 3-(4-phenylpiperazin-2-yl)- and especially 3-(4-benzylpiperazin-1-yl)-5-amino-1*H*-1,2,4-triazole to the corrosive environment causes a much more significant E_{corr} shift.

Table 2. Open circuit potential, polarization resistance, corrosion current density, and degree of protection of copper electrode in 0.01 M NaCl solutions with different derivatives of 5-amino-1*H*-1,2,4-triazole.

| Inhibitor	C_{inh}, mM	E_{corr}, V	R_p, kΩ·cm^2	i_{corr}, μA·cm^{-2}	Z_i, %
–	–	0.172	41.9±4.6	1.2±0.3	–
A	0.1	0.231	191±21	0.12±0.03	90
	1.0	0.221	266±46	0.13±0.04	89
B	0.1	0.210	69±9	0.46±0.09	62
	1.0	0.220	71±14	0.42±0.12	65
C	0.1	0.150	76±7	0.37±0.09	69
	1.0	0.260	120±22	0.33±0.11	73
D	0.1	0.260	46.5±8.4	0.53±0.11	56
	1.0	0.300	95±12	0.38±0.06	68

The polarization curves obtained for copper in chloride solution with addition of derivatives of 5-amino-1*H*-1,2,4-triazole are shown in Figures 1–4. It can be seen that the electrochemical behavior of copper in solution with addition of 3-(4-methylpiperazin-2-yl)-5-amino-1*H*-1,2,4-triazole (Figure 2) is noticeably different from the other systems. For instance, the anodic current density decreases regardless of the inhibitor concentration, but only at $E < 0.25$–0.30 V.
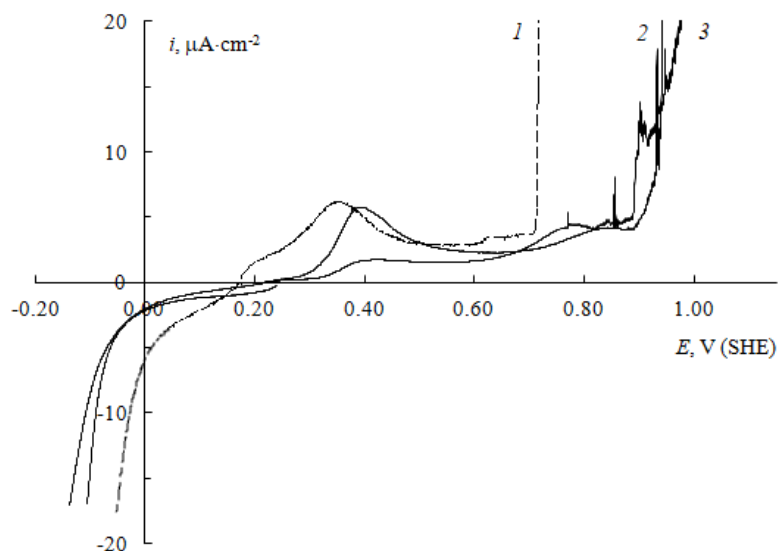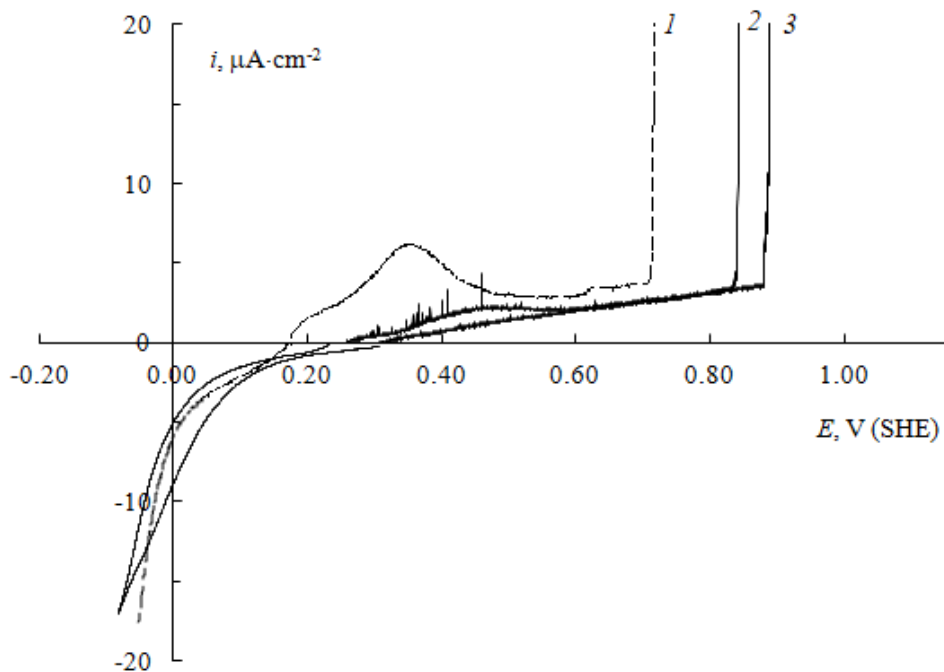

Figure 1. Anodic and cathodic polarization curves of copper in borate buffer (pH 7.4) + 10 mM NaCl without an inhibitor (*1*) and in the presence of 3-(piperidin-1-yl)-5-amino-1*H*-1,2,4-triazole (*2*–0.10 mM; *3*–1.00 mM).
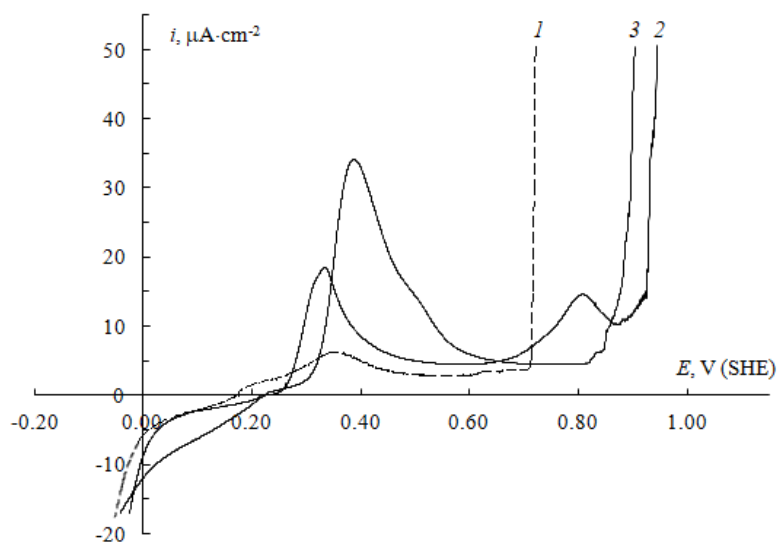
Figure 2. Anodic and cathodic polarization curves of copper in borate buffer (pH 7.4) + 10 mM NaCl without an inhibitor (*1*) and in the presence of 3-(4-methylpiperazin-2-yl)-5-amino-1*H*-1,2,4-triazole (*2*–0.10 mM; *3*–1.00 mM).
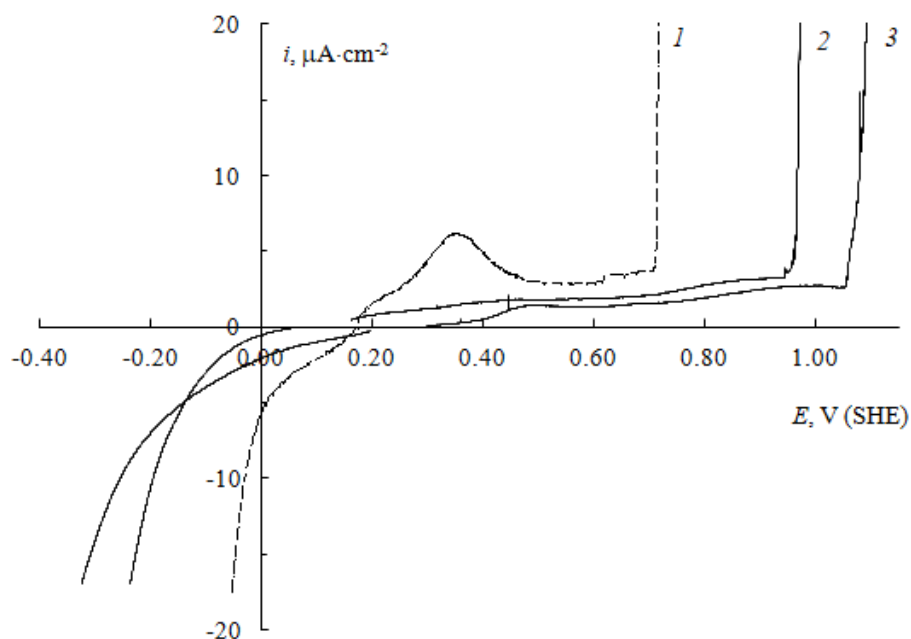
Figure 3. Anodic and cathodic polarization curves of copper in borate buffer (pH 7.4) + 10 mM NaCl without an inhibitor (*1*) and in the presence of 3-(4-phenylpiperazin-2-yl)-5-amino-1*H*-1,2,4-triazole (*2*–0.10 mM; *3*–1.00 mM).

Figure 4. Anodic and cathodic polarization curves of copper in borate buffer (pH 7.4) + 10 mM NaCl without an inhibitor (*1*) and in the presence of 3-(4-benzylpiperazin-1-yl)-5-amino-1*H*-1,2,4-triazole (*2*–0.10 mM; *3*–1.00 mM).

With further shift of the potential to the anodic region, the rate of copper oxidation in solutions containing an inhibiting additive becomes higher than in the background solution. At the same time, as the inhibitor concentration increases, an increase in the current and ennoblement of the potential of the anodic maximum is observed, and in the 0.1 mM solution of 3-(4-methylpiperazin-2-yl)-5-amino-1*H*-1,2,4-triazole an additional peak on the polarization curve is formed. The passivation current density exceeds the value recorded in the background solution. A sharp increase in current is observed at the activation potential, which increases by about 0.2 V when the inhibitor is added to the solution, regardless of the concentration of the additive. The rate of the cathodic process on copper in a chloride solution in the presence of 0.1 mM 3-(4-methylpiperazin-2-yl)-5-amino-1*H*-1,2,4-triazole is higher than in the absence of inhibitor. A noticeable decrease in the cathodic current, which becomes close to that recorded in the background solution, is observed only at $C_{\text{inh}} =$ 1 mM.

A significantly different electrochemical behavior is characteristic of copper in the presence of 3-(piperidin-1-yl)-, 3-(4-phenylpiperazin-2-yl)- and 3-(4-benzylpiperazin-1-yl)-derivatives of 5-amino-1*H*-1,2,4-triazole. Indeed, when they are added to the chloride solution, the rates of the cathodic process and anodic oxidation of copper decrease, regardless of the nature of an inhibiting additive and its concentration. The position of the region of increased cathodic current density is noticeably shifted in the negative direction relative to the background chloride solution; the effect is more pronounced at higher concentrations of inhibitors. At the same time, their influence on the rate of the anodic process has a number of features. For instance, in the presence of 3-(piperidin-1-yl)-5-amino-1*H*-1,2,4-triazole, the maximum on the anodic curve disappears only at a concentration of 1 mM (Figure 1), whereas in the case of 3-(4-phenylpiperazin-2-yl) and 3-(4-benzylpiperazin-1-yl)-5-amino-1*H*-1,2,4-triazoles the anodic peak on the polarization curve is not formed already at a concentration of 0.1 mM (Figures 3 and 4). For all these additives, the passivation current density of the copper electrode decreases noticeably. Similarly to the 3-(4-methylpiperazin-2-yl)-derivative, the concentration of 3-(piperidin-1-yl)-5-amino-1*H*-1,2,4-triazole added to the chloride solution does not affect the activation potential E_{pit}, which, however, is already about 0.23 V higher than the value in the background solution. At the same time, in the case of 3-(4-phenylpiperazin-2-yl)- and 3-(4-benzylpiperazin-1-yl)-5-amino-1*H*-1,2,4-triazoles, along with a sharp slowdown of the anodic process, there is a significant increase in the pitting potential, which strongly depends on the inhibitor concentration and reaches ~1.08 V in 1 mM solution of 3-(4-benzylpiperazin-1-yl)-5-amino-1*H*-1,2,4-triazole.

Analysis of the values of the corrosion current density determined by the polarization resistance method (Table 2) allows us to conclude that the all the compounds studied containing a heterocyclic substituent in the third position of the aminotriazole cycle have a low but acceptable protection degree of at least 56%. Moreover, if piperazine derivatives of 5-amino-1*H*-1,2,4-triazole are characterized by similar values of Z_i (on average 60–70%),

then addition of 3-(piperidin-1-yl)-5-amino-1*H*-1,2,4-triazole to the chloride solution provides a noticeably higher protective effect ($Z_i \sim 90\%$).

The low inhibitory effect of the aminotriazoles investigated with respect to copper corrosion identified during electrochemical studies was confirmed by corrosion tests. The degree of protection against acid corrosion for all inhibitors was 30–60% (Table 3). With increasing concentration of the inhibitor, this parameter as a whole increases. The greatest protective effect in 1% aqueous solution of HCl was again shown by 3-(piperidin-1-yl)-5-amino-1*H*-1,2,4-triazole, for which the inhibition coefficient was $\gamma \sim 2$ already at 1 mM. At the same time, none of the inhibitors was effective in atmospheric corrosion of copper: the time of onset of the first signs of corrosion did not exceed 40–60 hours, which is not a good result.
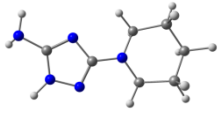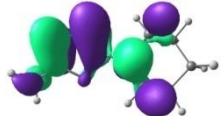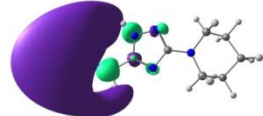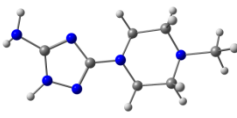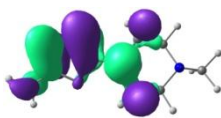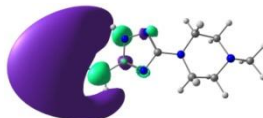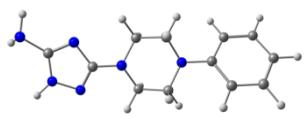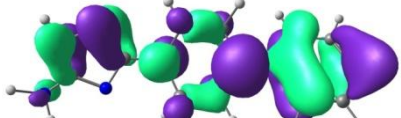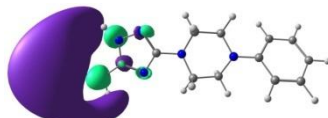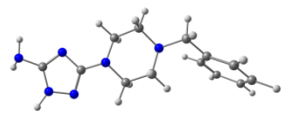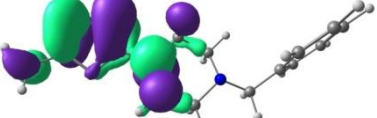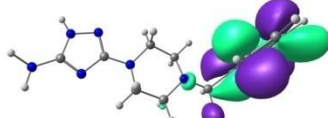
Table 3. Results of the copper corrosion tests.

Inhibitor	C_{inh}, mM	k, g·m^2·day^{-1}	γ	Z_k, %	τ_{corr}, h
	1	22.1	1.99	49.7	36
A	5	18.1	2.43	58.8	40
	10	30.6	1.44	30.5	43
	1	29.9	1.47	32.1	38
B	5	28.6	1.54	35.1	38
	10	25.9	1.70	41.2	40
	1	28.0	1.57	36.4	42
C	5	28.3	1.56	35.7	42
	10	21.7	2.03	50.6	57
	1	29.7	1.48	32.5	38
D	5	29.1	1.51	33.8	40
	10	25.3	1.74	42.5	43

The results of electrochemical studies and corrosion tests are interpreted in the framework of the quantum-chemical approach to the evaluation of the inhibitory effect. The geometric and electronic structures of 3-hetarylamino-5-aminotriazole inhibitors were calculated by optimizing their bond lengths, bond angles and dihedral angles. The optimized molecular structures and the frontier molecular orbital pictures of the molecules are shown in Table 4.

Quantum chemical parameters are obtained from the calculations which are responsible for the inhibition efficiency of inhibitors such as the energies of frontier molecular orbitals (E_{HOMO}) and (E_{LUMO}), the separation energy $E_{\text{LUMO}} - E_{\text{HOMO}}$, representing the function of reactivity, and softness (σ). The data are presented in Table 5 and Figure 5.

**Table 4.** The optimized molecular structures of the 3-hetaryl-5-amino-1*H*-1,2,4-triazoles.

Optimized molecular structure	HOMO	LUMO
(A)		
(B)		
(C)		
(D)		

E_{HOMO} is a quantum chemical descriptor which is often associated with the electron donating ability of the molecule. High value of E_{HOMO} likely indicates a tendency of the molecule to donate electrons to appropriate acceptor molecule of low empty molecular orbital energy. Therefore, E_{LUMO} indicates the ability of the molecule to accept electrons. Thus, the lower the value of E_{LUMO}, the more probable the molecule accepts electrons [37]. The binding ability of the inhibitor to the metal surface increases with increase in the HOMO and decrease in the LUMO energy values. The calculated quantum chemical parameters show that the inhibitor **A** (3-(piperidin-1-yl)-5-amino-1*H*-1,2,4-triazole) has the lowest separation energy $E_{LUMO}-E_{HOMO} = 4.93$ eV among the investigated 3-hetaryl-5-amino-1*H*-1,2,4-triazoles, which means the highest reactivity of the inhibitor towards the metal surface and hence the highest inhibition efficiency. Also, the calculations show that it has the highest value for softness σ, which could increase its inhibition efficiency.

Table 5. Calculated Ionization Potential (IP), Electron Affinity (EA), and Softness (σ) in eV at B3LYP/6-311+ G (d, p) optimized geometry.

Molecule	E_{HOMO}	E_{LUMO}	IP	EA	σ
A	−5.35	−0.42	5.35	0.42	0.41
B	−5.43	−0.45	5.43	0.45	0.40
C	−5.51	−0.52	5.51	0.52	0.40
D	−5.45	−0.47	5.45	0.47	0.40

The effect of piperazine substituents on the frontier molecular orbitals leads to an increase in the separation energy $E_{LUMO} - E_{HOMO}$ (Figure 5). This indicates the lowering reactivity of inhibitors B, C, and D towards the metal surface and decreasing its inhibition efficiency. The calculations show that the softness is slightly decreased which is probably responsible for the decrease in its adsorption on the metal surface. Accordingly, the investigated inhibitors can be classified depending on their quantum chemical parameters as follows: inhibitor (A) > inhibitor (B) ≈ inhibitor (C) ≈ inhibitor (D). This order is in good agreement with the experimental results.
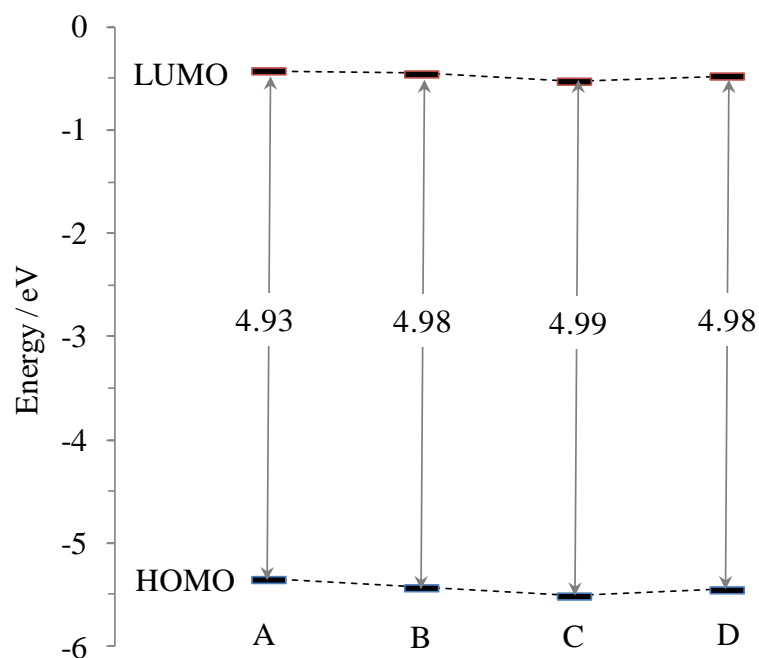
Figure 5. Correlation diagram of frontier molecular orbitals for the investigated inhibitors and their calculated $E_{LUMO} - E_{HOMO}$ (eV).

Conclusion

Addition of the *N*-hetaryl derivatives of 5-amino-1*H*-1,2,4-triazole studied to a borate buffer solution in the presence of 10 mM NaCl leads to an increase in the pitting potential of copper electrode. Addition of 3-(piperidin-1-yl)-, 3-(4-phenylpiperazin-2-yl)- and 3-(4-benzylpiperazin-1-yl)-5-amino-1*H*-1,2,4-triazoles to the solution slows down the electrode processes on the copper surface. The inhibitors studied are characterized by a low degree of copper protection in neutral and acidic chloride-containing corrosive environments, which grows with increasing inhibitor concentration in solution. 3-(Piperidin-1-yl)-5-amino-1*H*-1,2,4-triazole is characterized by the maximum protective effect, which is justified using quantum-chemical DFT simulations. None of the inhibitors studied is effective against atmospheric corrosion of copper.

Int. J. Corros. Scale Inhib., 2019, **8**, no. 2, 422–436

434

Acknowledgements

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