
Triazoles as a class of multifunctional corrosion inhibitors. Review. Part V. 1*H*-1,2,4-Triazole and its derivatives. Copper and its alloys

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Abstract

This article continues the review of studies (2007–2022) on organic corrosion inhibitors (OCIs) of the triazole class and their effect on the corrosion–electrochemical behavior of Cu and some of its alloys. In contrast to the first three reviews of this series, which devoted to the analysis of the corrosion inhibiting properties of 1,2,3-benzotriazole (BTA) and its derivatives, this article is devoted to another large group of OCIs of the triazole class, the parents of which are 1*H*-1,2,4-triazole (TA). In this article an important role is assigned to the study of the adsorption of TA and its derivatives from a neutral solution on the Cu surfaces at a constant electrode potential. In these works, the highly sensitive *in situ* reflective ellipsometry method was widely used. It made it possible to measure the adsorption isotherms of the OCIs under study and to determine from them the standard free energy of adsorption of these compounds on copper or its alloy. In addition to measuring the adsorption of OCI and the results of direct corrosion tests in aggressive neutral chloride solutions containing various concentrations of triazoles and their derivatives, the possibility of using known fungicides with an appropriate chemical structure as copper OCI is discussed. Of great interest is the technique of self-assembly of well-ordered organic films on metal, which in recent years has shown itself to be a very promising and controllable method of anticorrosion protection. Click-chemistry reactions, the synthesis of 1,2,3-triazole, catalyzed not only by Cu(I) cations but also by their complexes, are considered. Examples of effective protection of copper and its alloys from corrosion in hydrochloric, sulfuric, and even nitric acid solutions are also discussed.

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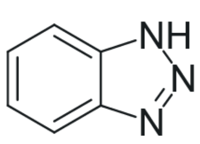
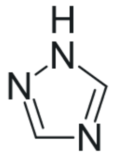
Introduction

1*H*-1,2,4-Triazole (TA) as an organic corrosion inhibitor (OCI) of Cu and its alloys has long been known, as well as 1,2,3-benzotriazole (BTA). It has valuable biological properties, such as antimicrobial and antibacterial, sedative, hypoglycemic, anti-inflammatory, anti-tuberculosis, *etc.* [1]. Antifungal drugs often include chemical compounds containing a 1,2,4-triazole moiety in their structure. Several fungicides containing a 1,2,4-triazole nucleus are in demand for plant protection in agriculture, and therefore are produced on an industrial scale. It is not surprising that not only TA, but also its derivatives attracted the attention of researchers in the field of anticorrosion protection in the search of an alternative to BTA and other similar OCIs for protecting primarily copper and its alloys.

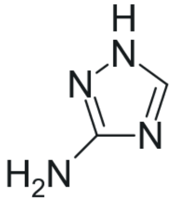
Of the substituted TAs, aminotriazoles and their derivatives have been the most widely studied. These OCIs are interesting in that they are better soluble in water than BTA, *i.e.* being relatively hydrophilic chemical compounds, they are little inferior, and sometimes even superior to it in the protective ability in relation to a metal or alloy.



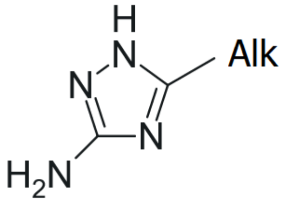
BTA



TA



ATA



5-Alkyl-ATA

Triazole isomers (TA with pK_a 10.0 [2] and 1*H*-1,2,3-triazole with pK_a 9.4 [4]) are weaker NH acids than BTA (pK_a 8.4), but, as quantum-chemical calculations have shown that their adsorption from aqueous solutions on Cu is more likely not in the molecular, but in the anionic form [4]. In this case, it is logical to evaluate the hydrophobic (hydrophilic) properties of OCIs by the value of $\log D$, which is calculated according to the equation [5]:

$$\log D = \log P - \log[1 + 10^{(\mathrm{pH} - \mathrm{p}K\mathrm{a})}]$$

where $\log P$ is the logarithm of the distribution coefficient of a chemical compound in a system of two immiscible liquids, octanol–water is taken as its criterion Hansch hydrophobicity parameter; pH refers to a specific aqueous solution. For example, for an aqueous solution of borate buffer with pH 7.4, in which corrosion and electrochemical studies are often carried out, $\log D$ differs little from $\log P$ for BTA, TA and ATA and are equal to 1.30, –0.58 and –1.06; respectively. Note that even 5-pentyl-ATA with pH 10.18 remains less hydrophobic than BTA, since its $\log P \approx \log D = 1.13$. As will be shown below, this compound certainly outperforms BTA in adsorption capacity on copper.

There are many review articles in the scientific literature, in which a large place is occupied by studies of the effectiveness of corrosion inhibition of Cu and its alloys, as well as the study of the features of the mechanism of their protection by BTA, TA or their substituted ones [1, 4, 6–15]. According to the authors of [1], TA and many of its derivatives are often able to slow down corrosion in various environments of Cu, Zn, Fe, and Al. Their low toxicity and high chemical activity, due to amphoteric properties and the presence of three nitrogen atoms in the composition, capable of interacting with metals, open up the possibility of forming the strong bonds between OCI and the protected surface.

I. Triazoles

Adsorption of OCIs, including triazoles, is usually the first and very important act of their interaction with the protected metal surface. Since the corrosion of metals in aqueous solutions is an electrochemical process, it is important to measure the adsorption of OCI in such a medium by the *in situ* method on electrodes, the potential (E) of which is maintained (controlled) by a special device – a potentiostat. Such measurements were carried out in the mid-1980s by the method of reflection ellipsometry in studies of the adsorption passivation of iron or low-carbon steel in borate buffer solutions (pH 7.4) by the salts of higher carboxylic acids [16]. Later, the techniques developed by us were transferred in the study of OCIs adsorption on various metals (Fe, Cu, Zn, Ni, Au, Mg), steels, and some alloys.

Neutral media

The adsorption of triazoles on pre-oxidized (passive) Cu was studied at a constant potential $E = 0.0$ V [16]. The angles Δ and Ψ were measured on a hand-held ellipsometer RR2000 in a cell used for simultaneous electrochemical and ellipsometric measurements. The radiation source was a helium–neon laser with a wavelength $\lambda = 640$ nm, the angle of incidence of the light beam on the sample was 68.5°. Before the start of measurements, the electrode for the reduction of the oxide formed on it in the atmosphere was kept for 30–40 min in a borate buffer at $E = -0.6$ V, then the potential was abruptly shifted to $E = 0.0$ V, at which, according to the Pourbaix diagram, the following equilibrium was established

$$2Cu + H_2O = Cu_2O + 2H^+ + 2e^- \qquad (1a)$$

$$E = 0.471 - 0.059\,pH \qquad (1b)$$

After 30 min of such exposure of the electrode in the solution, the ellipsometric angles stop changing, which indicates stabilization of the Cu_2O oxide film. By adding concentrate CI (C) to the cell in portions, we obtained the dependence of the change in the phase shift angle $\delta\Delta = -\alpha(\Delta - \Delta_0)$ on $\lg C$, which is proportional to the thin adsorption film thickness d:

$$d = \alpha\delta\Delta = -\alpha(\Delta - \Delta_0) \qquad (2)$$

where α is the coefficient of proportionality, Δ_0 and Δ are the values of the phase shift angle, respectively, before and after the addition of the adsorbate to the solution, *i.e.* angle measured in time. It is usually accepted that if $\delta\Delta < 0$, then the film d increases, and if $\delta\Delta > 0$, the film becomes thinner. In the first case, such changes in the angle Δ indicate film growth or OCI adsorption, and in the second case, a decrease in its d or adsorbate desorption.

When the angle Δ ceases to change with the addition of the next portion of OCI, it is assumed that the degree of surface coverage with the adsorbate (Θ) tends to 1. This allows us to consider the obtained dependence as an adsorption isotherm of the studied triazole. Figure 1a shows dependences (2) obtained by the authors for BTA [17], 3-ATA and 4-amino-1,2,4-triazole (4-ATA) [18], and Figure 1b shows their adsorption isotherms, adequately described in the region of average fillings by the Frumkin equation:

$$BC = [\Theta/(1 - \Theta)]\exp(-2a\Theta), \tag{3}$$

where B is the adsorption equilibrium constant related to the standard free energy of adsorption by the relation $B = [\exp(-\Delta G_a^0 / \mathrm{RT}] / 55.5$; C is the adsorbate concentration, a is the attraction constant characterizing the interaction between adsorbate particles.

All the obtained functions $\delta\Delta = f(\log C)$ are characterized by the same shape of curves with a pronounced plateau, which indicates the formation of a monolayer filling of the surface with an adsorbate. However, a subsequent increase in C does not make it possible to achieve an equilibrium state of adsorption in time. This may be due to the insufficient continuity of the monolayer coating and the gradual formation of a complex compound of triazole with Cu(I) on its defects, which was observed by many authors using various methods for BTA and was repeatedly discussed in reviews, including ours [3, 6, 13]. Differences in adsorption between BTA and more hydrophilic aminotriazoles are small, although, as follows from the characteristics of substituted triazoles in Table 1, in which the set of substituted triazoles is expanded, with a decrease in hydrophilicity or an increase in their hydrophobicity, the value $(-\Delta G_a^0)$ increases in the series: 4-ATA < 3-ATA < TA < 5-pentyl-3-ATA < 5-mercaptopentyl-3-ATA. Why BTA is not included in such a qualitative correlation is not yet completely clear; it is possible that this is due to the spatial effects of this OCI during adsorption. This assumption is supported by the well-known fact that bulky substituents in the adsorbate molecule, although they increase the surface activity of the compound, can hinder adsorption or the formation of its complex compound with copper.

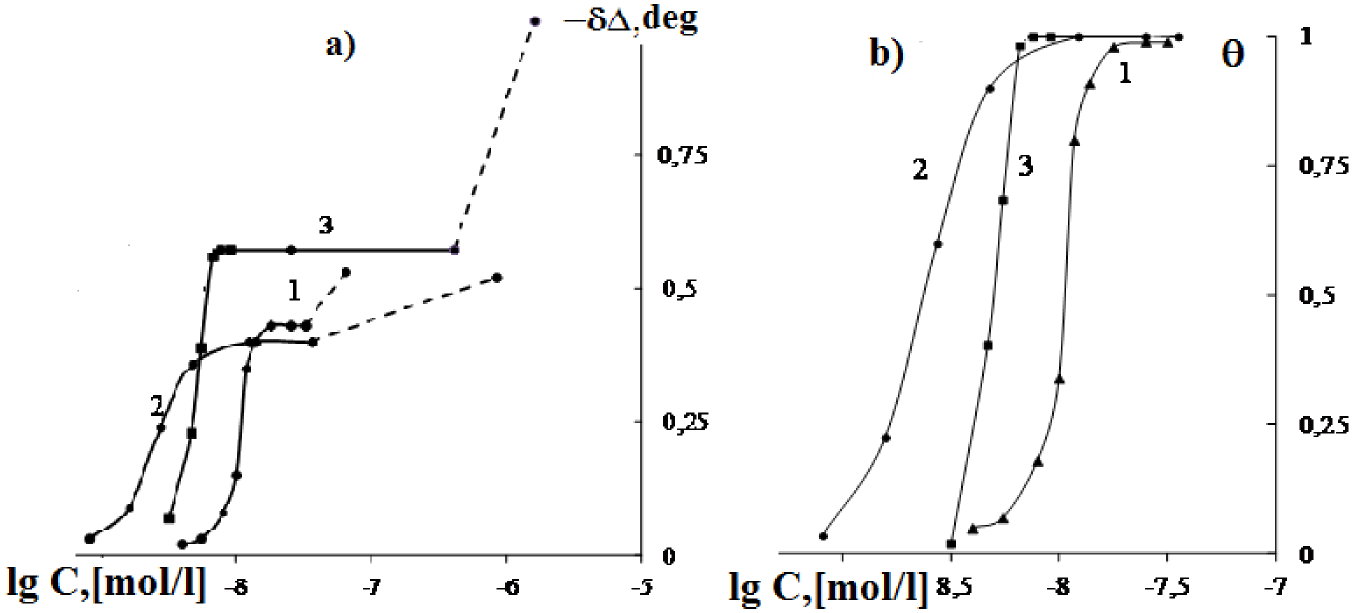


Figure 1. Change in the ellipsometric angle Δ on the concentration of triazoles in borate buffer with pH 7.4 (a) and the adsorption isotherms (b) of: BTA (1), 3-AT (2) and 4-AT (3) on the copper surface at E = 0.0 V. The dotted lines on the curves show the regions of nonstationary values of the angle.

Table 1. Dependence of hydrophobicity characteristics ($\lg P$, $\lg D$) and standard free energies of adsorption of triazoles ($-\Delta G_a^0$) on their chemical structure.

OCI characteristics	BTA	4-ATA	3-ATA	TA	5-pentyl-3-ATA	5-mercaptopentyl-3-ATA
$\lg P$	1.34	–1.38	–0.87	–0.58	1.13	2.17
$\lg D$	1.30	–1.38	–0.87	–0.58	1.13	2.16
$(-\Delta G_a^0)$, kJ/mol	50.5±0.5	51.3±2.6	53.5±2.7	64.0±2.8	69.0±3.4	70.1±3.5
Value *a*	1.7±0.1	2.0±0.2	1.3±0.2	1.7±0.2	1.8±0.2	1.9±0.3
d monolayer, nm		0.5±0.1	0.36±0.1			
References	[17]	[3]	[3]	[3, 18]	[3, 18]	[3,18]

*The values of hydrophobicity characteristics were calculated using the ACD-Lab program on the Internet resource https://ilab.acdlabs.com. $\lg D$ values are taken for pH 7.40.

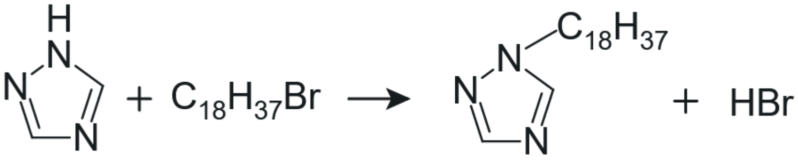
At the same time, all the above triazoles, including BTA, are adsorbed on oxidized copper with a sufficiently high value $(-\Delta G_a^0) > 40$ kJ/mol, which gives reason to believe that their interaction with the metal surface has a chemisorption nature.

Ellipsometric measurements make it possible to determine the thicknesses of the monolayers of the studied triazoles on oxidized copper [3]. Having determined the coefficient α in equation (2) and the corresponding changes in the ellipsometric angles for the monolayer filling of the surface with OCIs, one can obtain their thicknesses: for 1*H*-1,2,4-triazole ($-\delta\Delta = 0.310$), $d = 0.28 \pm 0.1$ nm, 5-pentylmercapto-3-ATA ($-\delta\Delta = 0.400$), $d = 0.36 \pm 0.1$ nm, for pentyl-3-ATA ($-\delta\Delta = 0.280$), $d = 0.25 \pm 0.1$ nm.

If we take into account that the size of TA molecules is 0.36 nm, then it can be assumed that its particles in the adsorbed state are located in a position almost vertical to the electrode surface. The size of 5-pentyl-3-ATA (1.24 nm) or 5-pentylmercapto-3-ATA (1.38 nm) molecules is so much larger than the thickness of their monolayers that it is reasonable to assume that their state in the adsorbed state on the surface is close to horizontal, *i.e.* flat.

The values of the attraction constant *a* in the adsorption isotherm equations do not differ much for the triazoles under consideration. However, it can be noted that the most attractive interaction between adsorbate molecules is observed for 4-ATA, which, although it is characterized by the highest hydrophilicity, but it is not an NH-acid due to the presence of an $>N-NH_2$ bond. A change in the position of the amino group in the triazole ring of 3-ATA reduces not only the hydrophilicity, but also the attractive interaction between its particles.

The presence of alkyl or mercaptoalkyl in 3-ATA derivatives increases the hydrophobicity of their molecules and slightly increases the coefficient a. It is not surprising that the introduction of a long alkyl (C_{18}) into the TA molecule to the >NH group in its heterocycle according to the reaction [19]:



significantly increases the lg*P*, adsorption, and protective properties of the new OCI. This compound, 4-octadecyl-TA (ODTA), like 4-ATA, lacks the properties of an NH-acid, but has much more hydrophobic properties ($\lg P = 8.1 \pm 0.2$). In other works, Appa Rao *et al.* [20, 21] showed that self-assemble films (SAM) of 2-(octadecylthio)benzothiazole or 1-octadecyl-1*H*-imidazole on copper obtained from organic solvents (from ethyl acetate and methanol), have a high efficiency of metal corrosion protection in sodium chloride solutions.

The value of the contact angle of wetting the copper surface with a water drop (Θ) without and with SAM ODTA is 78° and 104°, respectively, which was quite expected, since ODTA itself is characterized by high hydrophobicity. The hydrophobicity of the ODTA film turned out to be higher than when the copper surface was modified by adsorption with 2-(octadecylthiobenzothiazole) [20] or 1-octadecyl-1*H*-imidazole [21].

ODTA was only relatively soluble in methanol (maximum 15 mmol/L), so its SAM was applied from this solvent [19]. The copper sample was preliminarily polished and etched for 30 s in 7.0 M HNO_3 to remove oxide from its surface, rinsed with water and an organic solvent, and then immersed in an ODTA methanol solution for different times (12–48 h). After that, the sample was washed successively with methanol and distilled water to remove weakly adsorbed ODTA molecules.

The study of surface morphology by atomic force microscopy (AFM) confirmed the decrease in the root meansquare roughness of copper from 17.275 nm for copper itself to 14.174 nm in the case of coating it with SAM ODTA. The XPS and FTIR spectra led the authors to the conclusion that ODTA molecules are chemisorbed on copper through the interaction of their nitrogen atoms with the metal surface and form chelate complexes with Cu(I).

Various electrochemical studies were carried out in aqueous solutions of NaCl with a concentration of $C = 0.02–0.20$ M in order to assess the stability of the formed ODTA film and its protective properties. Thus, cyclic voltammetry of copper, carried out in the *E* range from –0.40 to +0.35 V (relative to the Ag/AgCl/1 M KCl electrode) at a potential scanning rate of 30 mV/s, showed the stability of SAM even after 15 cycles. The polarization curves of the electrode with SAM showed effective inhibition of the cathodic reaction.

The study of the effect of ODTA concentration on the electrochemical impedance spectra (EIS) measured in an aqueous solution of 0.30 mmol/L NaCl allowed the authors to conclude that the optimal formation of SAM on a copper electrode occurs when it is formed in a methanol solution of 15 mmol/L OCI and the duration of immersion in such an electrode solution for 48 h.

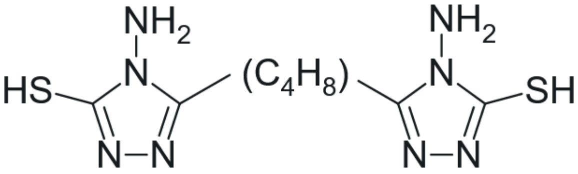
Relatively long-term corrosion tests (10 days) by immersing copper samples in an aqueous solution of 0.02 M NaCl and measuring the weight loss showed that in the absence of a coating, the corrosion rate reaches 0.0641 mm/year, but when SAM is present on the sample, it decreases by almost 18 times (0.0036 mm/year). These results confirm the high performance of the protective film as indicated by the accelerated EIS test results.

Other hydrophobic derivatives of TA also have high protective properties with respect to copper. For example, El-S.M. Sherif *et al.* [22] synthesized and studied as OCI for copper (99.999% Cu) 5-Phenyl-4*H*-1,2,4-triazole-3-thiol (PTAT) characterized by $\lg P = 2.23 \pm 0.64$, in aqueous 3.5% NaCl solution. They found that this compound was a mixed type OCI as it slowed down both electrode reactions on copper. The inhibitory effect, determined by the value of the polarization resistance, increases with time and after 100 hours complete suppression of copper dissolution is achieved if $C_{\text{in}} \geq 1.0$ g/L. Corrosion tests (even longer ones – 16 days) in a chloride solution confirm the effect of reducing the corrosion rate of copper, which was determined by the weight loss of the samples, over time, reaching even 90% at $C_{\text{in}} = 1.5$ g/L. Studies of the copper surface after its contact with a PTAT solution by Fourier transform infrared spectroscopy (FTIR) showed strong adsorption of this OCI on it.

PTAT, as shown in [23], can be successfully used in a 3% NaCl solution as an OCI not only to protect copper, but also tin bronze (wt.%: 92 Cu – 8 Sn). It slows down the cathodic reaction only at $C_{\text{in}} > 1.0$ mM; the anodic reaction of bronze dissolution is inhibited by it already at 0.1 mM. Having carried out polarization measurements and using the Stern–Geary equation to calculate the experimental results, the authors found that Z increased from 81.6 to 95.9% with an increase in C_{in} from 0.1 to 1.0 mM. Even better results are shown by EIS measurements, which at the same C_{in} show $Z = 98.8$ and 99.8%. Analysis of the bronze surface using scanning electron microscopy (SEM) and X-ray energy dispersion (EDS) showed the presence of sulfur on it. The use of Raman micro-spectrometry allowed the authors to state that the protective effect of PTAT in a chloride solution is due to three types of its interaction with the electrode: its adsorption with a flat molecule configuration, the formation of copper-thiol molecules, and when copper is released, a polymer complex is formed.

It should be noted that the PTAT molecule contains not only a hydrophobic aromatic phenyl, but also a very active sulfur-containing group. As shown by the authors of [24], when studying the protection of copper with the addition of 3-methyl-1,2,4-triazole-5-thione (MTS) in an aqueous solution of 3% NaCl containing up to 10 ppm Na_2S, this OCI demonstrates high efficiency, despite its significantly lower hydrophobicity ($\lg P = 0.43 \pm 0.56$) than PTAT. MTS is a mixed type OCI, achieving a protection degree of $Z = 90\%$ in solution with a low $C_{\text{in}} = 10$ mmol/L. This value of Z deserves attention, since the protection of copper with other triazoles (BTA and its derivatives) is very sensitive to the presence of sulfide anions in the corrosive medium [13]. The results of measurements of the EIS of a copper electrode in an MTS solution led the authors to the assumption that a very thin film with dielectric properties and a complex composition, including the corrosion product of copper and MTS, is formed on its surface.

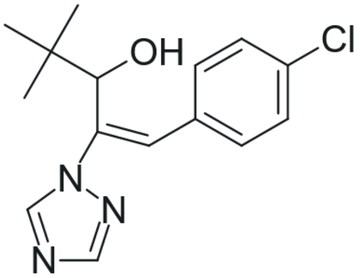
Another TA derivative, bis-(4-amino-5-mercapto-1,2,4-triazol-3-yl)-butane (bis-(4-amino-5-mercapto-1,2,4-triazol-3-yl)-butane BAMTB) containing two SH groups:



was reported [25]. BAMTB was shown to be an excellent OCI in such a solution and more effective than BTA. Judging by the polarization measurements, it is a mixed-type OCI, since it slows down the rates of both electrode reactions. The effectiveness of this OCI increases with the duration of copper immersion in the solution and with C_{in} up to 8.9 mmol/L, *i.e.* to the limiting solubility of OCI in an aqueous solution.

The anticorrosive effect of BAMTB towards copper in 3% NaCl is due to the formation of a thin (several nanometers) but very protective film on active surface areas. It prevents the formation of copper chloride, cuprite and atacamite. Using Raman spectroscopy and EDX analysis, the authors concluded that BAMTB interact with the surface of the copper electrode through the sulfur atom, which leads to the formation of a thiol complex.

Another group of triazole derivatives are relatively low-toxic fungicides that have the ability to slow down the corrosion of copper as well [26, 27, 29, 30]. For example, the well-known fungicide 1-(4-chlorophenyl)-4,4-dimethyl-2-(1,2,4-triazol-1-yl)-1-penten-3-ol (uniconazole),



can rapidly biodegrade into non-toxic compounds [26]. In this regard, N. Tian *et al.* [27] conducted studies including quantum-chemical calculations of uniconazole adsorption on copper, measurements of its corrosion rate by various methods (polarization curves, gravimetric and EIS), as well as the study of surface morphology using scanning electron microscopy (SEM) and X-ray EDS.

As shown by quantum chemical calculations, electron densities are concentrated around heteroatoms (N, O, Cl) and conjugated double bonds. It is assumed that OCI forms a chelate on the copper surface due to the transfer of electrons from the organic molecule to the metal. This creates the possibility of the formation of a covalent bond during chemisorption. Authors suggested that the adsorption of uniconazole on copper may occur due to the interaction of frontal orbitals. Having considered the density distribution of frontier orbitals of uniconazole molecules, the authors came to the conclusion that its planar structure must be very active with several possible adsorbed centres for interaction with the metal.

Corrosion and electrochemical measurements were carried out in an aqueous solution of 3.5% NaCl at $t = 25°C$ and uniconazole concentration $C_{in} = 1–20$ mg/L. Working solutions were prepared from a microemulsion of 2% uniconazole. To do this, first 2 g of substituted triazole was mixed with cyclohexanone, and then 44 g of OP-10 emulsifier (Tianjin DaMao Energizing Chemistry) was added to this mixture. The prepared mixture was weighed, and then the required dose of the emulsion was added to a 3.5% NaCl solution. When investigating the effect of C_{in} on the corrosion rate of copper (99.99% Cu) in 3.5% NaCl, the pH was maintained at 7.5. It is shown that already at $C_{in} = 1$ mg/L, the value of Z, depending on the method of measuring corrosion, was in the case of polarization, gravimetric and EIS methods (in %): 85.2, 76.7 and 81.4. Copper protection increased with an increase in C_{in} up to 20 mg/L, when Z (in %), respectively, reached 96.9; 94.7 and 97.5. When studying the role of pH in the range of its value from 5.5 to 8.5 $C_{in} = 5$ mg/L, the inhibitory effect of uniconazole increases with increasing pH 5.5; 6.5; 7.5 and 8.5, in this case, Z (in %) calculated from the mass loss of the sample is 81.4; 88.6; 92.1 and 94.8, respectively.

Noteworthy are the results of studying the effect of solution temperature on the protective effect of uniconazole. The range of studied temperatures varied at pH 7.5 and $C_{in} = 10$ mg/L from 25° to 55°C. It turned out that the degree of protection of copper with uniconazole additives decreases with increasing temperature, and at $t = 25°$, 35°, 45° and 55°C the value of Z (in %) is 98.1, 90.8, 89.3 and 81.9, respectively.

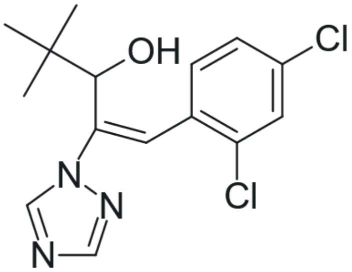
The authors also evaluated the adsorption of uniconazole on copper, based on the calculation of its adsorption isotherm, constructed from the results of electrochemical and corrosion (by sample mass loss) measurements. Previously, the riskiness of assessing adsorption based on the results of direct corrosion measurements was already discussed earlier by the editors of our journal [28]. A more reliable way is to measure the adsorption of OCI on metals by the EIS method, which makes it possible to determine the dependence of the electric double layer capacitance, C_{dl}, on the adsorbate concentration and construct an adsorption isotherm. The authors found that in both cases the adsorption of uniconazole is adequately described by the Langmuir equation:

$$BC = \Theta/(1 - \Theta) \tag{4}$$

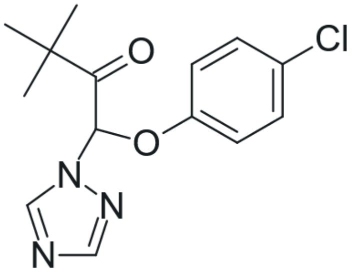
The value ($-\Delta G_a^0$) of unicanazole calculated from the constant B, determined from measurements of the corrosion rate of copper, is 45.3 kJ/mol, and EI is slightly less than 44.2 kJ/mol. The authors concluded that uniconazole chemisorbs on copper. However, it is difficult to reconcile with this conclusion the decrease in the protection of copper with uniconazole, not only according to corrosion data, but also the results of EIS, even with a slight increase in the temperature of the solution.

Another example of the successful use of biocides as OCIs to protect copper in an aqueous solution of 3.5% NaCl, simulating sea water, is 1-(2,4-dichlorophenyl)-4,4-dimethyl-2-(1,2,4-triazole-1-yl)-1-pentenyl-3-ol), *i.e.* dinico-nazole ($\lg P = 4.26 \pm 0.64$) and

(1-(4-chlorophenoxy-3,3-dimethyl-1-(1*H*-1,2,4-triazol-1-yl)-2-butanone, *i.e.* triadimefon ($\lg P = 2.77 \pm 0.89$) [29].



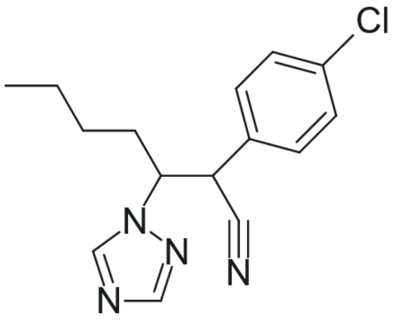
Diniconazole



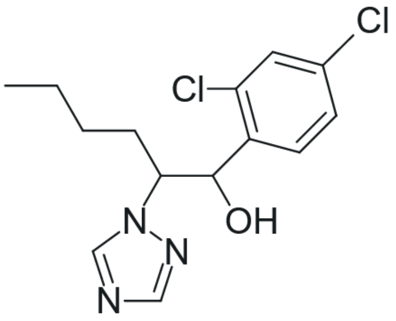
Triadimefon

These compounds are mixed type OCIs because they slow down both electrode reactions. They are introduced into the chloride solution in the form of an emulsion, which was described above [29]. Diniconazole is noticeably superior in hydrophobicity not only to triadimefon, but also to uniconazole ($\lg P = 3.84 \pm 0.63$). At $C_{\text{in}} = 20$ mg/L, in the efficiency of copper protection, diniconazole surpasses triadimefon in all three methods of its measurement: $Z = 91.1\%$ (gravimetric), 94.9% (polarization) and 97.9% (EIS) (respectively, $Z = 88.0\%$; 90.6% and 93.3%). However, it is slightly inferior to uniconazole, surpassing it only in the EIS results ($Z = 99.2\%$).

Later, the attention of Chinese researchers [30] was attracted by two more fungicides for effective protection of copper from corrosion in a 3.5% NaCl solution: myclobutanil, 2-(4-chlorophenyl)-2-(4*H*-1,2,4-triazole-1-ylmethyl) hexanenitrile and hexaconazole, 2-(2,4-dichlorophenyl)-1-(4*H*-1,2,4-triazole-4-yl)hexan-2-ol. Of particular interest is hexaconazole, which, undergoing photocatalytic transformations in the studies of P. Calza *et al.* [31], not only itself, but also the stable products of its reactions, for example, cyanuric acid, do not have acute toxicity.



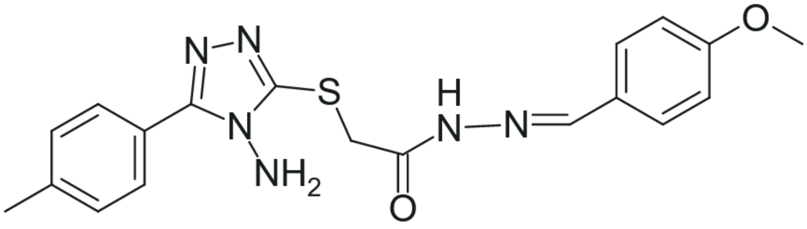
Myclobutanil



Hexaconazole

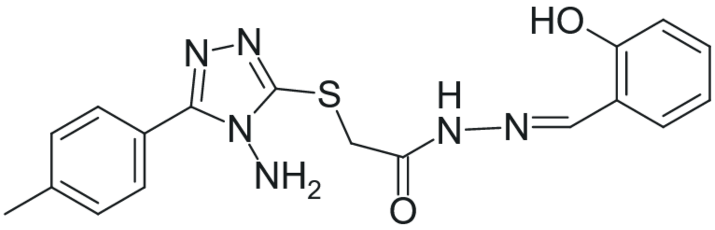
It turned out that these compounds are very effective OCIs of copper in a 3.5% NaCl solution, especially hexaconazole ($\lg P = 3.66 \pm 0.56$), which at a very low $C_{\text{in}} = 0.5$ mg/L provides a significant value of Z, when corrosion rate measured by three methods (gravimetric – 86.7%, polarization – 91.2% and EIS – 86.7%). Increasing C_{in} to 1.5 mg/L allows one to increase Z to 96.8, 98.7 and 98.5%, respectively. It has also been shown that both OCIs are more effective in solutions with pH 6.5–7.5 than even in slightly acidic (pH 5.5) or slightly alkaline (pH 8.5) media. As in the articles discussed above, the authors, having evaluated the adsorption of hexaconazole by three methods, found that it is adequately described by the Langmuir isotherm equation with the value $(-\Delta G_a^0) = 47.2$–48.2 kJ/mol. They explained this by chemisorption of this OCI on copper. Unfortunately, even for hexoconazole, a slight increase in the temperature of the solution (by 10°C) adversely affects its protective effect.

H. Tian *et al*. [32] developed new OCIs, which are triazolyl-acylhydrazone derivatives, to protect copper from corrosion in 1.0 M NaCl solutions:



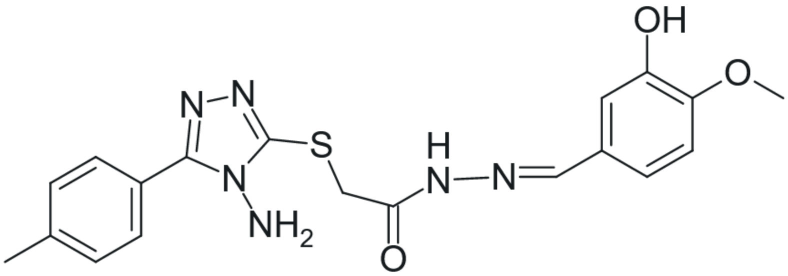
ATA

Anisaldehyde-[5-(p-methyl)-phenyl-4-amino(1,2,4-triazolyl)-2-thiol]-acylhydrazone



STA

Salicylal-[5-(p-methyl)-phenyl-4-amino(1,2,4-triazolyl)-2-thiol]acylhydrazone



VTA

Vanillin-[5-(p-methyl)-phenyl-4-amino(1,2,4-triazolyl)-2-thiol]acylhydrazone

These compounds, in addition to aminotriazole fragments, include groups that allow them to be classified as acylhydrazone compounds, which can act as very active ligands and form multiadsorption structures with metal atoms [33]. Some transition metal complexes with acylhydrazones appear to be excellent OCIs, and natural aldehyde groups containing *p*-electrons and electronegative heteroatoms also have a strong adsorption capacity on metal surfaces. The authors of [32] considered it very important to combine the active adsorption sites of these compounds in order for the synthesized OCIs to acquire a high efficiency of copper protection under severe corrosive conditions. They synthesized three new OCIs: STA, ATA, and VTA containing multifunctional groups such as aminotriazole, natural aldehyde, and thiol acylhydrazone.

Electrochemical and corrosion studies were carried out on electrodes and samples made of pure copper (99.999% Cu). These OCIs do provide a high level of protection for copper in chloride solution and it does not degrade after several cycles of alternating between wet and dry samples. At the same time, they are OCIs of a mixed type, slowing down both electrode reactions. The effectiveness of protection at the same C_{in} increases in the series: VTA>STA>ATA.

In solutions of these OCIs, the copper surface is covered with an adsorption film, which in all three cases has hydrophobic properties with $\Theta_c = 115°$. The adsorption of OCIs is adequately described by the Langmuir–Freundlich adsorbing isotherm model. The authors came to the conclusion that physical adsorption and chemisorption simultaneously take place on copper, which nevertheless dominates. Of the three OCIs, VTA has the highest packing density of OCI molecules in a film on the copper surface, and its adsorption film is more uniform than that of the other two OCIs. Although the aromatic ring and aliphatic hydrocarbon chain contained in OCI molecules do not participate in chemisorption on copper, C=N in the triazole ring, C=S binds to the triazole ring, and the C=O and C=N stretching vibrations of the acylhydrazone group form multidentate, chemisorption bonds with the Cu surface.

Like BTA, TA or its substitutes can be used as OCIs in suspensions used in chemical-mechanical polishing of Cu. It was shown in [34] that the addition of 45 mM TA to a suspension of 0.1 wt.% colloidal silica provides protection against corrosion of the copper surface, similar in effectiveness to 2.0 mM BTA. In this case, the technological properties of the suspension are better, for example, less metal erosion than in the case of using a suspension with 1.0 mM BTA and 5.0 wt.% silica. The authors, having studied the mechanism of copper passivation with the help of TA, identified two ways of its implementation. One of them is the growth of a passivating Cu–TA film on the copper surface. The thickness of such a film can reach 60 nm, which was proved by XPS analysis of the copper surface after its treatment with a 20 mM TA solution with pH 6.0. Another way of passivation is the deposition of the Cu–TA complex on the oxidized copper surface. Such complexes are formed by copper ions entering the suspension during metal polishing, where they react with TA. As a result, nanoparticles of the Cu–TA complex are formed, which, in the form of a precipitate, cover the oxidized Cu surface, forming a weak film that complements the first "direct" growth path of the passivating film.

One of the important applications of copper in industry is its use as a structural material in heat exchangers, including desalination equipment for sea water. This is due to the high thermal conductivity and good mechanical properties of copper, but its significant drawback is insufficiently high corrosion resistance. In this regard, the self-assembly technique deserves attention for obtaining well-ordered organic films on the metal surface, which are very promising for anti-corrosion protection [35]. Due to the hydrophobic effect and intermolecular forces, molecular aggregations can form between OCI molecules, which affect the assembly of the molecule on the metal surface and the effectiveness of its protection against corrosion. Hence, the desire of researchers to create a controlled assembly method in order to facilitate it and thereby increase the effectiveness of protection.

An example of a click chemistry reaction is the synthesis of 1,2,3-triazole catalyzed by Cu(I) cations from azides and alkynes. It represents the best click chemistry paradigm due to its properties of high reaction yield, ease of reaction, and purification conditions [36]. In [37], the authors noted that although "the inhibitory effect of triazole compounds strongly depends on the degree of their polymerization, little attention has been paid to triazole SAMs assembled in situ on the copper surface." In this article, they used a click chemistry reaction to self-assemble the film (Figure 2), the main purpose of which was to inhibit copper corrosion:

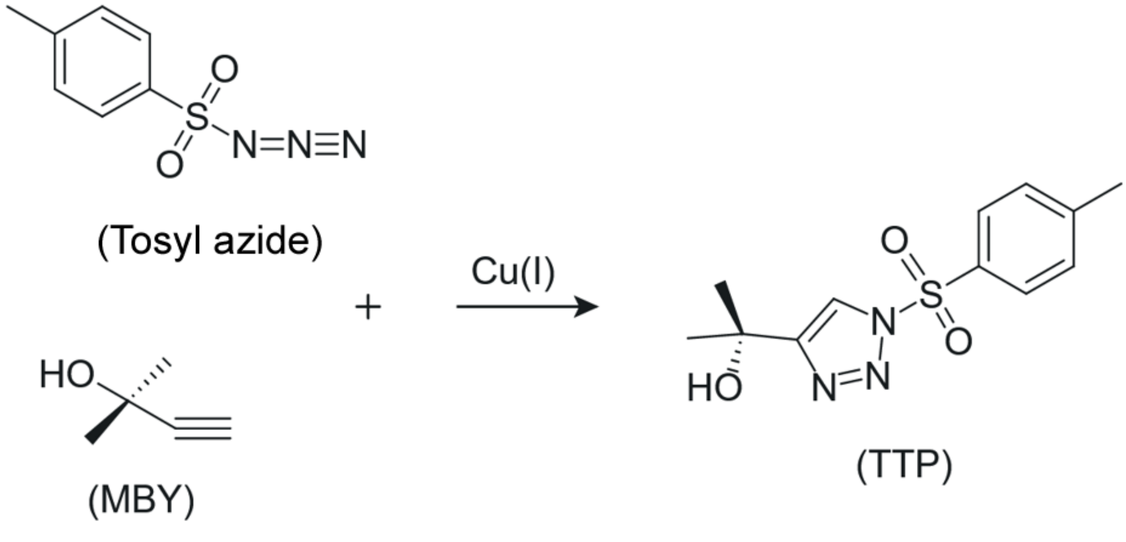


Figure 2. Click chemistry reaction equation of tosyl azid and MBY on the copper surface.

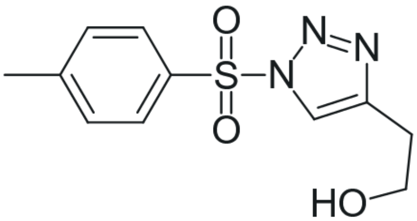
The reagents tosyl azide, 2-dimethylethynylcarbinol (MBY), and their mixtures (0.5 mM TA + 0.5 mM MBY) were used as ethanol solutions. Copper electrodes (99.99% Cu) were cleaned, degreased with ethanol, and washed with deionized H_2O. The electrodes were immersed in assembly solutions (in assembling solutions) for 1 h at room temperature.

After assembly, they were thoroughly washed with deionized water to remove physically adsorbed particles from the copper surface and dried with N_2. To confirm the formation of triazole on the surface of Cu, experiments were carried out with similarly prepared copper samples, studying their surface using FTIR in the reflection mode and comparing the obtained spectra with the IR absorption spectra of the pure compounds themselves. The dried electrodes were immersed in 3% NaCl solutions for 1 h, and the protective properties of the films were evaluated using the removed potentiodynamic polarization or EIS. The results of electrochemical measurements showed that the monolayer film of the synthesized (assembled on the copper surface) compound 2-(1-tosyl-1*H*-1,2,3-triazol-4-yl)propan-2-ol (TTP) facilitates the passivation of this metal , reaching in a very aggressive chloride environment $Z = 93.6\%$. TTP has better protection against copper corrosion than the original connections for its assembly.

To study the microrelief of the copper surface, the authors used scanning electron (SEM) and atomic force (AFM) microscopes. FT-IR was used to confirm the result of TTP assembly on the copper surface. To establish the relationship between the inhibition efficiency and its molecular structure, the authors also used quantum chemical calculations and MD simulations. They showed that TTP molecules are chemisorbed on the Cu_2O surface in a planar orientation.

The role of Cu(I) ions in the process of TTP assembly was continued in [38] by adding 150 μL of a saturated CuCl solution (≈0.009 mM) or 0.009 mM NaCl to the assembly solution of 3% NaCl. The attack of chloride ions on the surface of the copper electrode causes the appearance of Cu(I), which act as a catalyst for the formation of compact triazole films on the surface of the copper sample. This improves its protection against corrosion of copper in a 3% NaCl solution and suppresses the anodic reaction.

Later, K. Zhang *et al.* [39] used a click chemical reaction between *p*-toluenesulfonyl azide (TSA) with 3-butyne-1-ol (BTO) and sodium thioacetate (sodium thioacetate, STA) for the assembly of a film of substituted triazole TTE on the copper surface:



In contrast to the click reaction considered above, where Cu(I) cations served as a catalyst, this function was performed by the copper thioacetate complex STA–Cu(I) in the assembly of TTE. This made it possible to avoid the solvation reaction of Cu(I) in an aqueous solution, thereby increasing the efficiency of catalysis. In addition, STA has strong reducing ability, so it reacts with Cu(II) to form STA-Cu(I) complex and copper corrosion protection with TTE film. The film assembled in a solution of 2 mM STA + 40 mM TA + 40 mM WTO has the best efficiency of microdiprotection in 3% NaCl solution with $Z = 94.6\%$. The authors note the environmental friendliness of the assembly method and the simplicity of the technology due to the combination of self-assembly and click-chemical reaction. They see its originality and novelty in the replacement of the Cu(I) catalyst with its STA-Cu(I) complex, which keeps Cu(I) on the copper surface, which gives the technology the advantages listed above.

Acidic solutions

Of course, TA and its derivatives in acids are not as widely studied and used as in neutral media. S. El Issami *et al.* [40] found that TA additives in 0.5 M HCl slow down the corrosion of copper very little in 0.5 M HCl even at $C_{\text{in}} = 0.01$ M. However, the same concentration of 3-ATA significantly slows down the cathodic reaction and corrosion of copper, although it is inferior in efficiency to 3,5-diamino-1,2,4-triazole (DTA). Later, the authors of [41] showed that neither 3-ATA nor 3-amino-5-mercapto-1,2,4-triazole (AMTA) are efficient OCI of the copper alloy (97.35 Cu – 2.57 Zn), as indicated by the results long-term corrosion tests (7 days) in a hydrochloric acid solution with pH 0.2 (0.1 M HCl + 0.1 M acidic potassium phthalate) with pH 0.2 and a temperature of 300°C, at least at $C_{\text{in}} \leq 300$ ppm $Z \leq 68.9\%$. The alloy is slightly better protected under these conditions by 3-amino-5-methylthio-1,2,4-triazole (AMTT), which provides $Z = 78.3\%$ at $C_{\text{in}} = 100$ ppm. It was possible to increase the protection of the alloy by a small addition (10 ppm) of a cationic surfactant – cetyltrimethylammonium bromide (CTAB) to 100 ppm of triazoles: with ATA $Z = 89.7\%$, AMT – 91.1%, AMTT – 91.2%), although CTAB itself even at 20 ppm does not reach $Z > 57\%$. Anionic surfactant – sodium dodecyl sulfate (SDS), which itself provides $Z = 66.35\%$ at 2500 ppm in a composition with 100 ppm AMTT reaches $Z = 93.32\%$. The polarization curves of the alloy showed that these acidic OCIs retard both electrode reactions. The authors also concluded that the studied combinations of triasoles with surfactants demonstrate synergistic protection of the copper alloy.

Moroccan researchers compared the inhibitory effect of 0.01 M TA, ATA, and DTA on copper corrosion in 0.5 M HCl with the results of quantum chemical calculations using the semiempirical theory of molecular orbitals [42]. ATA and DTA have been investigated in more detail as they have proven to be the best OCIs. Gravimetric and electrochemical measurements were carried out. A correlation has been obtained between the efficiency of copper corrosion inhibition and the calculated characteristic of OCI molecules, *i.e.* energy of the highest occupied molecular orbital of triazoles E_{HOMO}, which is often considered as a measure of the electron-donating ability of OCI. This allowed the authors to conclude that the calculation of the energy levels of molecular orbitals can be used to explain the order of efficiency of OCIs.

To elucidate the mechanism of copper corrosion inhibition in 0.5 M HCl solutions containing OCI, UV spectroscopic measurements of solutions were carried out before and after corrosion experiments. They showed that copper protection is accompanied by the formation of the Cu(I)-triazole complex.

E.M. Sherif [43] also studied the corrosion behavior of copper (99.999% Cu) when etched it in 0.5 M HCl and the corrosion inhibition of 3-ATA and AMTA. Methods used in these studies were mass loss determinations of samples, potentiodynamic polarization, chronoamperometry, EIS and Raman spectroscopy. It is shown that copper quickly dissolves in hydrochloric acid solution and the mass loss of the sample increases with time. 3-ATA and especially AMTA noticeably reduce these mass losses and the corrosion rate of copper, while the inhibitory effect of triazoles enhances with increasing their concentration in solution. This conclusion was also confirmed by electrochemical methods. Raman spectroscopy detection of 3-ATA and AMTA molecules on the surface of copper preliminarily kept for 48 h in a 0.5 M HCl solution containing 5 mmol/L triazole confirmed that copper protection is achieved due to the strong adsorption of OCI molecules on the sample surface and its ability to prevent the formation of copper chlorides and oxychloride complex compounds.

The authors of [44] studied the possibility of effective corrosion inhibition of copper (99.99% Cu) in a 0.5 M HCl solution using three substituted TA that contained 4-amino and 3-mercapto groups (Figure 3):

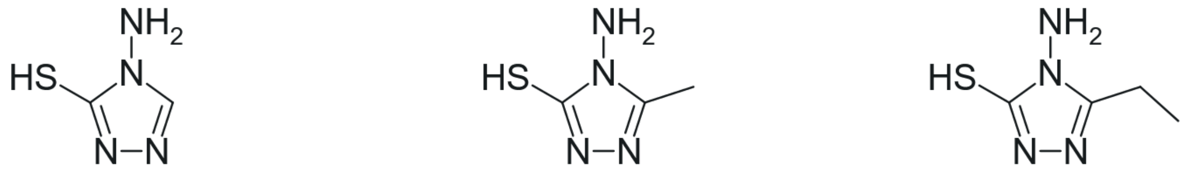
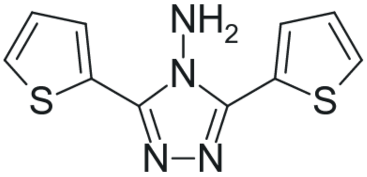

4-amino-4H-1,2,4-triazole-3-thiole (ATT)
4-amino-5-methyl-4H-1,2,4-triazole-3-thiole (AMTT)
4-amino-5-ethyl-4H-1,2,4-triazole-3-thiole (AETT)

Figure 3. Molecular structure of substituted TA.

They also used electrochemical and gravimetric corrosion methods to evaluate the effectiveness of OCIs, as well as quantum chemical calculations. It turned out that all the studied substituted triazoles are OCIs of the cathode type, and the most effective of them is AETT. Quantum-chemical calculations performed by the DFT method made it possible to calculate the energies of the highest occupied molecular orbital E_{HOMO} and the lowest unoccupied molecular orbital E_{LUMO} of the molecules of the studied molecules and to determine the dependence of the activity of triazoles on their chemical structure. According to the results of electrochemical measurements, the efficiency of copper protection by them increases in the series: ATT < AMTT < AETT. In the same order, the degree of protection of copper against corrosion, calculated from the mass loss of the samples at $C_{\mathrm{in}} = 2.58$ mM (in %), increases: and the difference $\Delta E = E_{\mathrm{LUMO}} - E_{\mathrm{HOMO}}$ decreases. It is noted that the value of the dipole moment of the molecules of these triazoles also decreases in the series: ATT(5.46) – AMTT(5.41) – AETT(5.17), and measured at $C_{\mathrm{in}} = 2.58$ mM, unfortunately, in a small temperature range (303–318)°K, the activation energy of copper corrosion E_a (in kJ/mol) increases in the series: without OCI (28.99) – ATT (51.61) – AMTT (58.24) –

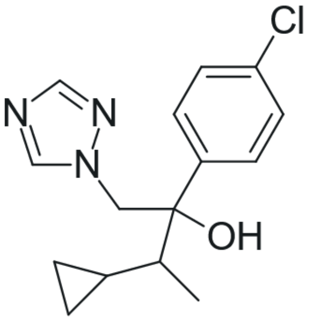
AETT (63.18). An analysis of the totality of the obtained data led the authors to the conclusion that the results of quantum-chemical and experimental studies are in good agreement with each other.

The authors of [45] studied the corrosion inhibition of copper (99.9% Cu) by 3,5-bis(2-thienyl)-4-amino-1,2,4-triazole (2-TAT) in solutions of 1 M HCl and 0.5 M H_2SO_4 at $t = 25°–40°C$. Potentiodynamic polarization curves of copper and EIS measurements were performed in acid solutions containing various concentrations of 2-TAT ($\log P = 2.71$):



2-TAT has a more efficient OCI in 1.0 M HCl (at $C_{in} = 6$ mmol/L $Z = 96\%$) than in 0.5 M H_2SO_4 (at $C_{in} = 6$ mmol/L $Z = 90.3\%$). In hydrochloric acid it is a cathode-type OCI in 1.0 M HCl, but in 0.5 M H_2SO_4 it is characterized as a mixed OCI. Although the influence of temperature on the rate of copper dissolution was evaluated over a small range of solution temperatures, the authors calculated the copper corrosion energy E_a. It turned out that E_a increased from 86.6 kJ/mol to 107.1 kJ/mol when 2 mmol/L 2-TAT was introduced into the 1 M HCl solution. In 0.5 M H_2SO_4, E_a almost did not change in the presence of this OCI in the acid solution (45.7 and 46.3 kJ/mol, respectively). The EIS measurement was used to study the adsorption of 2-TAT, adequately described by the equations of the Langmuir isotherm with the values of standard free energy adsorption calculated from it $(-\Delta G_a^0) = 37.9$ and 35.8 kJ/mol, for 1.0 M HCl and 0.5 M H_2SO_4, respectively.

Another OCI for copper in sulfuric acid solution was proposed by Chinese researchers [46]. Cyproconazole (CPA) is one of the azole fungicides, which is easily biodegradable, so it can be non-toxic OCI and applied in practice in industrial metal pickling processes. The molecular structure of CPA namely 2-(4-chlorophenyl)-3-cyclopropyl-1-(1*H*-1,2,4-triazol-1-yl)butan-2-ol (CPA) is shown below:



The effect of CPA on the corrosion resistance of pure copper (99.999% Cu) at 0.5 M was evaluated using potentiodynamic polarization and SEM. Potentiodynamic polarization curves were measured starting from the cathode potential $E = -0.25$ V (relative to SCE) to $E = +0.25$ V (relative to the open circuit potential) at a sweep rate of 0.5 mV/s. Polarization measurements were carried out in 0.5 M H_2SO_4 without and with the addition of CPA in the range $C_{\text{in}} = (0.01–1.0)$ mM and $t = (15–30)$°C. EIS was measured in the same range of C_{in} and t. The values of the degree of protection of copper against corrosion Z (in %), calculated from the polarization curves, showed that with an increase in the content in the solution, CPA always increases and is maximum at $t = 25$°C and $C_{\text{in}} = 1.0$ mM, reaching 98.3%. The polarization curves showed that CPA is a mixed type OCI, *i.e.* slows down both electrode reactions. At the same C_{in}, measurements showed that Z reaches 89.3, 91.3, 94.1 and 85.6% at 15, 20, 25 and 300°C, respectively.

The adsorption of CPA on copper was studied by the EIS method and shown to be described by the Dhar–Flory–Huggins substitution isotherm equations:

$$KC = \frac{\theta}{\exp(X-1)(1-\theta)^{X}} \tag{3}$$

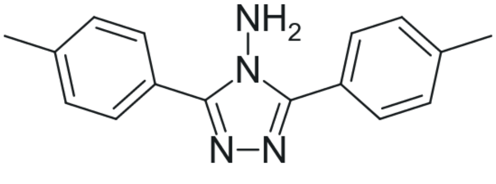
and Bockris–Swinkels:

$$KC = \frac{\theta}{(1-\theta)^{X}} \frac{[\theta + X(1-\theta)]^{(X-1)}}{X^{X}}, \tag{4}$$

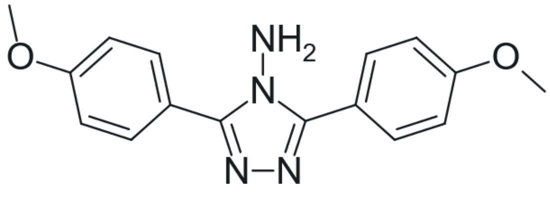
where K is the adsorption constant, C is the adsorbate concentrate, θ is the degree of filling of the adsorbent surface by it, X is the number of water molecules with the adsorbate.

It was found that at 25°C one CPA molecule replaces two water molecules. According to eq. 3, the value $(-\Delta G_{\text{a}}^{0}) = 46.2$ kJ/mol, an eq. 4 – 43.1 kJ/mol. The authors came to the conclusion that CPA is capable of interacting with copper through the mechanism of not only physical adsorption, but and chemisorption.

M.E. Belghiti *et al.* [47] studied the features of copper corrosion inhibition in 1.0 M HCl with two 3,5-disubstituted-4-amino-1,2,4-triazoles for copper corrosion were performed by EIS and scanning electron microscopy (SEM):



3,5-Bis-(4-methylphenel)-4-amino-1,2,4-triazole (MeAT)

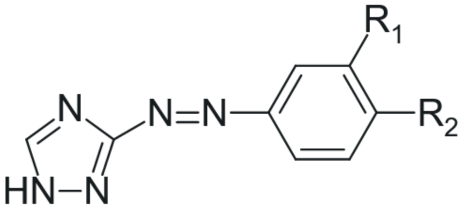


3,5-Bis-(4-methoxyphenyl)-4-amino-1,2,4-triazole (MxAT)

A comparative study of MeAT and MxAT was carried out and the influence of substituents on the characteristics of these OCIs was discussed. Simulation of the dielectric data was also performed for MxAT to closely monitor the change in dielectric constant. It was shown that the studied TA derivatives are relatively efficient copper OCIs in 1.0 M HCl. For example, MxAT at $t = 30°C$ and $C_{in} = 1.0$ mM provides $Z = 87.9\%$. It has been shown that the adsorption of MxAT on copper is well described by the Langmuir isotherm equation with the value $(-\Delta G_a^0) = 42.88$ kJ/mol), which gave the authors reason to associate its corrosion protection with OCI chemisorption.

Computational studies by DFT and Monte Carlo (MC) simulations were performed to search for correlations between inhibitory properties and quantum chemical parameters of the studied OCIs. DFT calculations were performed for the unprotonated and protonated forms of both OCIs (MeAT and MxAT), which provided a good picture of the interaction of inhibitors with copper and agreement with the experimental results. MC modeling has been considered as an effective tool for studying the behavior of Cu–inhibitor complexes. MeAT and MxAT molecules can be directly adsorbed on the substrate due to donor-acceptor interactions of inhibitors with the copper surface.

It is known that TA derivatives can be used as OCl in nitric acid solutions [48–51]. For example, L.H. Madkour *et al.* [48], investigated the possibility of inhibiting the corrosion of copper foil (99.99% Cu) containing 0.001% Pb as an impurity, in 0.5 M HNO_3 at various $t = 22°C–73°C$. As OSIs, they used three azo-heterocyclic dyes of the general formula (AT):



$D_1 = R_1 = CHO$; $R_2 = OH$
$D_2 = R_1 = OH$; $R_2 = CH_3$
$D_3 = R_1 = OH$

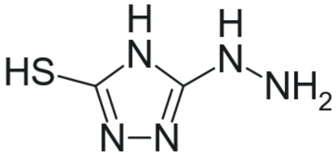
Here D_1 is 3-(3-formyl-4-hydroxy-l-phenylazo)-l,2,4-triazole; D_2 is 3-(2-hydroxy-5-methyl-l-phenylazo)-l,2,4-triazole; D_3 is 3-(4-hydroxy-l-phenylazo)-l,2,4-triazole.

The authors used potentiodynamic polarization to determine the change in the electrochemical characteristics of copper depending on the temperature, the presence AT and its composition and concentration in the solution. They found that ATs are good OCIs, and their protective effect is due mainly to the inhibition of the cathodic electrochemical reaction. Interestingly, in this case, the adsorption of OCl and the formation of Cu(II)–AT complex compounds on the surface of the copper electrode play an important role in this process.

The study of the effect of temperature on the electrochemical characteristics of copper in the presence of each of the three ATs in nitric acid showed that D_2 is the most effective of them, and the activation energy of copper corrosion at $C_{in} = 0.1$ mM increases in the series:

D_1 (65.79 kJ/mol) < D_3 (71.75 kJ/mol) < D_2 (128.64 kJ/mol). In addition, D_2 slows down the anodic dissolution of copper much more strongly; so it is a mixed type inhibitor.

Another example is considered in the article [49], in which the authors studied the efficiency of corrosion inhibition of copper (99.5% Cu) in a solution of 2 M HNO_3 at 303°K with the addition of 4-amino-3-hydrazino-5-mercapto-1,2,4- triazole (AHMT):



The protective properties of the new OCI were evaluated by test results, measuring the mass loss of copper samples, as well as by EIS and DC electrode polarization methods. The results obtained showed that AHMT is a good OCI, the inhibition efficiency of which increases with the growth of C_{in}, and the degree of copper protection by it at $C_{in} = 10$ mM reaches $Z = 91.7\%$.

Comparing these results with those previously obtained in similar tests for copper protection with 3-ATA ($Z = 82.2\%$) and 3,5-diamino-1,2,4-triazole ($Z = 86.5\%$) [50, 51], the authors concluded that AHMT is the best OCI of this group. According to the results of polarization studies, AHMT is a mixed-type OCI.

The adsorption of OCI on copper in the Cu/AHMT/2.0 M HNO_3 system was studied at various $T = 303$–343°K. It was shown that it is adequately described at all studied temperatures by the Langmuir isotherm equation. The kinetic and adsorption parameters for copper/acid in the presence and absence of AHMT were evaluated and discussed. The thermodynamic parameters of adsorption showed that ANMT is adsorbed on the Cu surface as a result of an exothermic spontaneous process. The calculated values of $-\Delta G_a^0$ and ΔH_{ad} gave reason to believe that the mechanism of AHMT adsorption on the copper surface in 2.0 M HNO_3 solution consists mainly in its physical adsorption on copper.

References

1. N.P. Swathi, V.D.P. Alva and S. Samshuddin, A Review on 1,2,4-Triazole Derivatives as Corrosion Inhibitors, *J. Bio- Tribo-Corros.*, 2017, **3**, 42. doi: 10.1007/s40735-017-0102-3
2. C. Hanch and A. Leo, *Substituent Constants for Correlation Analysis in Chemistry and Biology*, Wiley-Interscience: New York, 1979, 339.
3. Yu.I. Kuznetsov, M.O. Agafonkina, Kh.S. Shikhaliev, N.P. Andreeva and A.Yu. Potapov, Adsorption and passivation of copper by triazoles in neutral aqueous solution, *Int. J. Corros. Scale Inhib.*, 2014, **3**, no. 2, 137–148 doi: 10.17675/2305-6894-2014-3-2-137-148

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4. G. Gece, The use of quantum chemical methods in corrosion inhibitor studies. Review, *Corros. Sci*., 2008, **50**, 2981–2992 doi: 10.1016/j.corsci.2008.08.043
5. R.A. Scherrer and S.M. Howard, Use of distribution coefficients in quantitative structure-activity relationships, *J. Med. Chem*., 1977, **20**, no. 1, 53–58. doi: 10.1021/jm00211a010
6. Yu.I. Kuznetsov and L.P. Podgornova, Ingibirovanie korrozii metallov geterotsiklilicheskimi khelatoreagentami (Inhibition of metals corrosion by heterocyclic chelate reagents), *Itogi Nauki Tekh., Ser.: Korroz. Zashch. Korroz. (Achievements of Science and Technology, Corrosion and Corrosion Protection)*, Moscow, VINITI, 1989, **15**, 132–184 (in Russian).
7. M.M. Antonijević and M.B. Petrović, Copper corrosion inhibitors. A review, *Int. J. Electrochem. Sci*., 2008, **3**, 1–28.
8. Yu.I. Kuznetsov and L.P. Kazansky, Physicochemical aspects of metal protection by azoles, *Russ. Chem. Rev*., 2008, **77**, no. 3, 219–232 doi: 10.1070/RC2008v077n03ABEH003753
9. M.M. Antonijević, S.M. Milić and M.B. Petrović Films formed on copper surface in chloride media in the presence of azoles, *Corros. Sci*., 2009, **51**, no. 6, 1128–1137. doi: 10.1016/j.corsci.2009.03.026
10. A. Kokalj, S. Peljhan, M. Finšgar and I. Milošev, What Determines the Inhibition Effectiveness of ATA, BTAH, and BTAOH Corrosion Inhibitors on Copper?, *J. Am. Chem. Soc*., 2010, **132**, 16657–16668. doi: 10.1021/ja107704y
11. M.B. Petrović Mihajlović and M.M. Antonijević, Copper Corrosion Inhibitors. Period 2008–2014. A Review, *Int. J. Electrochem. Sci*., 2015, **10**, 1027–1053.
12. N. Kovaćević and A. Kokalj, The relation between adsorption bonding and corrosion inhibition of azole molecules on copper, *Corros. Sci*., 2013, **73**, 7–17. doi: 10.1016/j.corsci.2013.03.016
13. Yu.I. Kuznetsov, Triazoles as a class of multifunctional corrosion inhibitors. A review. Part I. 1,2,3-Benzotriazole and its derivatives. Copper, zinc and their alloys, *Int. J. Corros. Scale Inhib*., 2018, **7**, no. 3, 271–307 doi: 10.17675/2305-6894-2018-7-3-1
14. Ẑ.Z. Tasić, M.B. Petrović Mihajlović, M.B. Radovanović and M.M. Antonijević, New trend in corrosion protection of copper, *Chem. Pap*., 2019, **73**, 2103–2132. doi: 10.1007/s11696-019-00774-1
15. A. Fateh, M. Aliofkhazraei and A.R. Rezvanian. Review of corrosive environments for copper and its corrosion inhibitors, *Arabian J. Chem*., 2020, **13**, 481–544. doi: 10.1016/j.arabic.2017.05.021
16. Yu.I. Kuznetsov, *Organic Inhibitors of Corrosion of Metals*, 1996, Plenum Press, New York, 283 p.
17. N.P. Andreeva, M.O. Agafonkina and Yu.I. Kuznetsov, Adsorption of 1,2,3-benzotriazole on copper from a borate buffer solution, *Korroz.: Mater., Zashch. (Corrosion: materials, protection)*, 2010, no. 9, 7–11 (In Russian).

18. Yu.I. Kuznetsov, M.O. Agafonkina and N.P. Andreeva. Inhibition of Copper Dissolution in Water Solutions of Triazoles, *Russ. J. Phys. Chem. A*, 2014, **88**, no. 4, 702–707. doi: 10.1134/S0036024414040141
19. B.V. Appa Rao, M.N. Reddy and B. Sreedhar, Self-assembled 1-octadecyl-1*H*-1,2,4-triazole films on copper for corrosion protection, *Prog. Org. Coat.*, 2014, **77**, 202–212. doi: 10.1016/j.porgcoat.2013.09.009
20. B.V. Appa Rao, Md. Yakub Iqbal and B. Sreedhar, Self-assembled monolayer of 2-(octadecylthio)benzothiazole for corrosion protection of copper, *Corros. Sci.*, 2009, **51**, 1441–1452. doi: 10.1016/j.corsci.2009.03.034
21. B.V. Appa Rao and M.N. Reddy, Formation and characterization and corrosion protection efficiency of self-assembled 1-octadecyl-1*H*-imidazole films on copper for corrosion protection, *Arabian J. Chem.*, 2017, **10**, S3270–S3283. doi: 10.1016/j.arabjc.2013.12.026
22. El-S.M. Sherif, A.M. El Shamy, M.M. Ramla and A.O.H. El Nazhawy, 5-(Phenyl)-4*H*-1,2,4-triazole-3-thiol as a corrosion inhibitor for copper in 3.5% NaCl solutions, *Mater. Chem. Phys.*, 2007, **102**, 231–239. doi: 10.1016/j.matchemhhys.2006.12.009
23. A. Dermaj, N. Hajjaji, S. Joiret, K. Rahmounia, A. Srhiri, H. Takenouti and V. Vivier, Electrochemical and spectroscopic evidences of corrosion inhibition of bronze by a triazole derivative, *Electrochim. Acta*, 2007. **52**, 4654–4662. doi: 10.1016/j.electacta.2007.01.068
24. K. Rahmouni, N. Hajjaji, M. Keddam, A. Srhiri and H. Takenouti, The inhibiting effect of 3-methyl-1,2,4-triazole-5-thione on corrosion of copper in 3% NaCl in presence of sulphide, *Electrochim. Acta*, 2007, **52**, 7519–7528.
25. Z. Khiati, A.A. Othman, M. Sanchez-Moreno, M.-C. Bernard, S. Joiret, E. Sutter and V. Vivier, Corrosion inhibition of copper in neutral chloride media by a novel derivative of 1,2,4-triazole, *Corros. Sci.*, 2011, **53**, no. 10, 3092–3099. doi: 10.1016/j.corsci.2011.05.042
26. S. Ramesh and S. Rajeswari, Evaluation of inhibitors and biocide on the corrosion control of copper in neutral aqueous environment, *Corros. Sci.*, 2005, **47**, 151–169. doi: 10.1016/j.corsci.2004.05.013
27. H. Tian, W. Li and B. Hou, Novel application of a hormone biosynthetic inhibitor for the corrosion resistance enhancement of copper in synthetic seawater, *Corros. Sci.*, 2011, **53**, 3435–3445. doi: 10.1016/j.corsci.2011.06.025
28. Yu.I. Kuznetsov, N.N. Andreev and S.S. Vesely, Why we reject papers with calculations of inhibitor adsorption based on data on protective effects, *Int. J. Corros. Scale Inhib.*, 2015, **4**, no. 2, 108–109.
29. L. Hu, Sh. Zhang, W. Li and B. Hou, Electrochemical and thermodynamic investigation of diniconazole and triadimefon as corrosion inhibitors for copper in synthetic seawater, *Corros. Sci.*, 2010, **52**, 2891–2896. doi: 10.1016/j.corsci.2010.04.038

30. W. Li, L. Hu, Sh. Zhang and B. Hou, Effects of two fungicides on the corrosion resistance of copper in 3.5% NaCl solution under various conditions, Corros. Sci., 2011, **53**, 735–745. doi: 10.1016/j.corsci.2010.11.006
31. P. Calza, C. Massolino and E. Pelizzetti, Photo-induced transformation of hexaconazole and dimethomorph over TiO_2 suspension, *J. Photochem. Photobiol., A*, 2008, **200**, no. 2–3, 356–363. doi: 10.1016/j.jphotochem.2008.08.018
32. H. Tian, Y.F. Cheng, W. Li and B. Hou, Triazolyl-acylhydrazone derivatives as novel inhibitors for copper corrosion in chloride solutions, *Corros. Sci.*, 2015, **100**, 341–352. doi: 10.1016/j.corsci.2015.08.022
33. S. Naskar, M. Corbella, A. Blake and S. Chattopadhyay, Versatility of 2,6-diacetylpyridine (dap) hydrazones in generating varied molecular architectures: synthesis and structural characterization of a binuclear double helical Zn(II) complex and a Mn(II) coordination polymer, *Dalton Trans.*, 2007, **21**, 1150–1159. doi: 10.1039/b615004g
34. L. Jiang, Y. Lan, Y. He, Y. Li, Y. Li and J. Luo, 1,2,4-Triazole as a corrosion inhibitor in copper chemical mechanical polishing, *Thin Solid Films*, 2014, **556**, 395–404. doi: 10.1016/j.tsf.2013.12.047
35. Z. Ghelichkhah, S. Sharifi-Asl, Kh. Farhadi, S. Banisaied, S. Ahmadi and D.D. Macdonald, L-cysteine/polydopamine nanoparticle-coatings for copper corrosion protection, *Corros. Sci.*, 2015, **91**, 129–139. doi: 10.1016/j.corsci.2014.11.011
36. L. Liang, D. Astruc, The copper(I)-catalyzed alkyne-azide cycloaddition (CuAAC) “click” reaction and its applications. An overview, *Coord. Chem. Rev.*, 2011, **255**, 2933–2945.
37. Y. Yu, Y. Wang, J. Li, D. Zhang and L. Gao, *In situ* click-assembling monolayers on Cu with enhanced corrosion resistance, *Corros. Sci.*, 2016, **113**, 133–144. doi: 10.1016/j.corsci.2016.10.016
38. Ch. Shi, Y. Wang, Y. Yu, J. Li, D. Zhang and L. Gao, The role of cuprous ions on the click-assembled triazole films against copper corrosion, *Corros. Sci.*, 2018, **145**, 100–108. doi: 10.1016/j.corsci.2018.09.019
39. K. Zhang, J. Lu, J. Li, D. Zhang, L. Gao and H. Zhouc, An improved approach to prepare triazole protective film by click-assembly on copper surface, *Corros. Sci.*, 2020, **164**, 108352. doi: 10.1016/j.corsci.2019.108352
40. S.El Issami, L. Bazzi, M. Hilali, R. Salghi and S. Kertit, Inhibition of copper corrosion in HCl 0.5 M medium by some triazolic compounds, In *Annales de Chimie, Science des Materiaux*, 2002, **27**, no. 4, 63–72.
41. A. Lalitha, S. Ramesh and S. Rajeswari, Surface protection of copper in acid medium by azoles and surfactants, *Electrochim. Acta*, 2005, **51**, 47–55. doi: 10.1016/j.electacta.2005.04.003
42. S. El Issami, L. Bazzi, M. Mihit, B. Hammouti, S. Kertit, E. Ait Addi and R. Salghi, Triazolic compounds as corrosion inhibitors for copper in hydrochloric acid, *Pigm. Resin Technol.*, 2007, **36**, no. 3, 161–168. doi: 10.1108/03699420710749027

43. E.M. Sherif, Corrosion behavior of copper in 0.5 M hydrochloric acid pickling solutions and its inhibition by 3-amino-1,2,4-triazole and 3-amino-5-mercapto-1,2,4-triazole, *Int. J. Electrochem. Sci*., 2012, **7**, 1884–1897.
44. Sudheer and M.A. Quraishi, Electrochemical and theoretical investigation of triazole derivatives on corrosion inhibition behaviour of copper in hydrochloric acid medium, *Corros. Sci*., 2013, **70**, 161–169. doi: 10.1016/j.corsci.2013.01.025
45. Y.-M. Tang, Y. Chen, W.-Z. Yang, X.-S. Yin, Y. Liu and J.-T. Wang, 3,5-Bis(2-thienyl)-4-amino-1,2,4-triazole as a corrosion inhibitor for copper in acidic media, *Anti-Corros. Methods Mater*., 2010, **57**, no. 5, 227–233. doi: 10.1108/00035591011075850
46. Z. Tao, W. He, S. Wang and G. Zhou, Electrochemical Study of Cyproconazole as a Novel Corrosion Inhibitor for Copper in Acidic Solution, *Ind. Eng. Chem. Res*., 2013, **52**, 17891–17899. doi: 10.1021/ie402693d
47. M.E. Belghiti, Y.El Ouadi, S. Echihi, A. Elmelouky, H. Outada, Y. Karzazi, M. Bakasse, C. Jama, A. Dafali and F. Bentiss, Anticorrosive properties of two 3,5-disubstituted-4-amino-1,2,4-triazole derivatives on copper in hydrochloric acid environment: Ac impedance, thermodynamic and computational investigations, *Surf. Interfaces*, 2020, **21**, 100692. doi: 10.1016/j.surfin.2020.100692
48. L.H. Madkour, M.A. Elmorsi and M.M. Ghoneim, Inhibition of Copper Corrosion by Arylazotriazoles in Nitric Acid Solution, *Monatsh. Chem*., 1995,·**126**, 1087–1095. doi: 10.1007/BF00811379
49. A. Zarrouk, B. Hammouti, A. Dafali and F. Bentiss, Inhibitive Properties and Adsorption of Purpald as a Corrosion Inhibitor for Copper in Nitric Acid Medium, *Ind. Eng. Chem. Res*., 2013, **52**, 2560–2568. doi: 10.1021/ie301465k
50. A. Zarrouk, B. Hammouti, H. Zarrok, M. Bouachrine, K.F. Khaled and S.S. Al-Deyab, Corrosion inhibition of copper in nitric acid solutions using a new triazole derivative, *Int. J. Electrochem. Sci*., 2012, **7**, 89–105.
51. A. Zarrouk, B. Hammouti, S.S. Al-Deyab, R. Salghi, H. Zarrok, C. Jama and F. Bentiss, Corrosion inhibition performance of 3,5-diamino-1,2,4-triazole for protection of copper in nitric acid solution, *Int. J. Electrochem. Sci*., 2012, **7**, 5997–6011.

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