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Inhibitive action of 3,4'-bi-1,2,4-Triazole on the corrosion of copper in NaCl 3% solution

A.Al Maofari [1,2], G. Ezznaydy[1], Y. Idouli, F. Guédira[1], S. Zaydoun[1], N. Labjar[1] and S. El Hajjaji[1]

[1]*Laboratoire S3ME, Faculté des Sciences, Université Med V, Morocco.*
[2]*Laboratoire de Physico-chimie, Faculté des Education, Lettre et Sciences,Université de Amran, Yemen*

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*Corresponding authors: E-mail: mofary66@yahoo.com, Tel: 0661303102

Abstract
The efficiency of a new corrosion inhibitor, the (bTA), on copper was investigated in an aerated 3% NaCl solution using various techniques by potentiodynamic polarisation techniques, weight loss measurements and surface analysis (SEM). Potentiodynamic polarization curves showed that (bTA) is a mixed-type inhibitor for copper in chloride solution 3% and is even more efficient than the reference compound benzotriazole. The inhibition efficiency was found to increase with concentration until 5×10^{-3}M. The maximal protection efficiency exceeded 94.65%.

Keywords: Corrosion, Inhibitor, Electrochemical, Copper, 1,2,4-Triazole.

1. Introduction
Organic compounds, mainly containing oxygen, nitrogen and sulfur atoms and having multiple bonds, are recognized as effective inhibitors of the corrosion of many metals and alloys. In different media, for a given metal, the efficiency of the inhibitor depends on the stability of the formed complex and the inhibitor molecule should have centres, which are capable of forming bonds with the metal surface via an electron transfer. Generally, a strong coordination bond causes higher inhibition efficiency, the inhibition increases in the sequence O<N<S<P [1-5]. The most widely used inhibitors in the field of copper corrosion in chloride containing media are azole derivatives. They have been [6 - 14] and still are the subject of numerous investigations, as shown by the publication of recent reviews [15, 16] in this domain.
Among the azole-type compounds, benzotriazole (BTA) [17-24] is the most used inhibitor from a practical point of view, because it shows very high inhibition efficiency in neutral-chloride containing aqueous solutions. In the case of BTA, it seems well established that it acts through the formation of a Cu(I)–BTA complex involving Cu–N bonds [25-27], but the number of N-atom involved in the bond, the orientation of the complex at the metal surface, and the influence of the benzenic ring on the inhibition efficiency are not completely understood. In order to increase the strength of bonding between copper(I) and the organic molecule, different azole derivatives were investigated, changing the number or position of substituent groups and the number of nitrogen atoms on the azole ring, or adding another heteroatom like sulfur [28,29]. For instance, 1,2,4-triazole [30-34] and its amino derivatives, tetrazole [24,31], thiadiazole [15,35,36], pyrazole [37,38], imidazole [39-41] and the corresponding derivatives have been suggested. These inhibitors have also been studied as corrosion inhibitors of copper based material such as bronzes [36, 42-44]. Nevertheless, to our best knowledge, the inhibition efficiency of BTA could not be improved up to now.
The aim of this paper is to present the remarkable inhibiting properties of a new corrosion inhibitor synthesized in our laboratory, as a derivative of 3,4'-bi-1,2,4-Triazole (3,4'-bi-1,2,4-triazole) (bTA) on the copper corrosion is investigated in an air saturated NaCl 3% solution, using electrochemical methods such as potentiodynamic polarisation techniques and weight loss measurements. The inhibition efficiency is followed as a function of immersion time at open-circuit potential, in the presence of four different inhibitor concentrations (10^{-4}, 5×10^{-4}, 10^{-3} and 5×10^{-3}M). Finally the mechanism of inhibition will be discussed from electrochemical results, SEM observations.

2. Experimental methods

2.1. Reagents

The corrosive medium was an aqueous aerated 3% NaCl solution prepared from bidistilled water. The 3,4'-bi-1,2,4-triazole (abbreviated as bTA) was prepared according to the method described by Willey and Hart [45]. The molecular structure was given in Fig. 1.

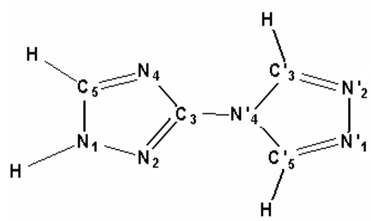

Figure 1. Molecule of 3,4'-bi-1,2,4-triazole.

2.2. Specimen and solutions preparation.

The electrode specimen was prepared from a square copper rod (99.99% purity) with a cross-section area of 2.8 cm^2. The electrode was mechanically ground with SiC abrasive papers (grade 400, 600, 1500 and 2000), washed by bidistilled water and then dried. The solution was NaCl 3% and the concentration range of bTA employed was varied from 10^{-4} M to 5×10^{-3} M.

2.3. Weight loss measurements

Gravimetric experiments were carried out in a double glass cell. The solution volume was 30 mL and experiments were performed with concentration of 5×10^{-3}M (bTA). The maximum duration of tests was 1 week (154h) at room temperature in aerated solutions. At the end of the tests, the specimens were carefully washed in distilled water and dried in hot air and then weighted. Duplicate experiments were performed in each case and the mean value of the weight loss is reported. Weight loss allowed calculation of inhibition efficiency of our extract according to the following equation:

$$E\% = \left(\frac{W° - W}{W°}\right) \times 100$$

Where W and W° are the weight loss of copper samples obtained in NaCl 3% solution in the presence and in the absence of inhibitor, respectively.

2.4. Electrochemical investigation

The measurements were carried out in a conventional three electrode cylindrical glass cell, containing 100 mL of electrolyte at room temperature. Platinum electrode was used as a counter electrode, a saturated calomel electrode (SCE) as the reference electrode and the working electrode was copper (99.99% purity). The potential scan rate was 500 µV/s. Cathodic and anodic polarisation curves were obtained separately starting from E_{corr} after a 60 min preliminary hold time.
The inhibition efficacy percent E% was calculated using the following equation:

$$E\% = \left(\frac{I^0 - I}{I^0}\right) x\, 100$$

Where $I^°$ and I are the corrosion current densities of copper in NaCl 3% in the absence and the presence of inhibitor, respectively.

2.5. Surface analysis

The surface morphology and chemical analysis of copper specimens after immersion in NaCl 3% solution for 158h in the absence and the presence of bTA were studied using a scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS).

3. Experimental results and discussion

3.1. Weight loss measurement

The corrosion rate and inhibition efficiency for copper in NaCl 3% media at room temperature in the absence and presence of bTA are given in Table 1. It is evident from these results that 5×10^{-3}M of bTA has an inhibition effect on corrosion of copper in NaCl 3%. The efficiency is stable according to the immersion time for 88 hours then increases to reach 85 % after 158h of immersion. This is due to an adsorption and a stability of the molecule on the copper surface.

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Table 1: Corrosion rate and efficiency data obtained from weight loss measurements for copper in NaCl 3% solution in the absence and the presence of bTA at 5×10^{-3}M.

Times (h)		22	44	88	110	132	154
W (mg $h^{-1}cm^{-2}$)	Blank	0.0613	0.075	0.087	0.105	0.1427	0.175
	bTA (5×10^{-3}M)	0.0125	0.0152	0.0193	0.0216	0.0231	0.0247
E%		79.61	79.68	77.82	79.43	83.81	85.89

3.2. Polarization measurements.

The effect of the concentration of bTA is shown in Fig.2, which presents the anodic and cathodic curves of copper in NaCl (3%) medium containing various inhibitor concentrations at room temperature. The anodic and the cathodic currents are significantly decreased in the presence of bTA for concentrations above 10^{-3}M. The electrochemical parameters were determined and presented in Table 2.

Table 2: Electrochemical parameters (E_{corr} and I_{corr}) and inhibitor efficiency, E(%), of the copper in NaCl 3% with and without inhibitors

Solutions	E_{corr}(V.ECS)	I_{corr}(A.cm^{-2})	E (%)
Blank	-0.187	6.6×10^{-5}	-
bTA (10^{-4}M)	-0.229	1.17×10^{-5}	82.27
bTA (5×10^{-4}M)	-0.252	6.89×10^{-6}	89.56
bTA (10^{-3}M)	-0.252	5.84×10^{-6}	91.15
bTA (5×10^{-3}M)	-0.252	3.54×10^{-6}	94.63

The simultaneous decrease of both anodic and cathodic current densities in presence of bTA shows that it behaves like a mixed inhibitor.

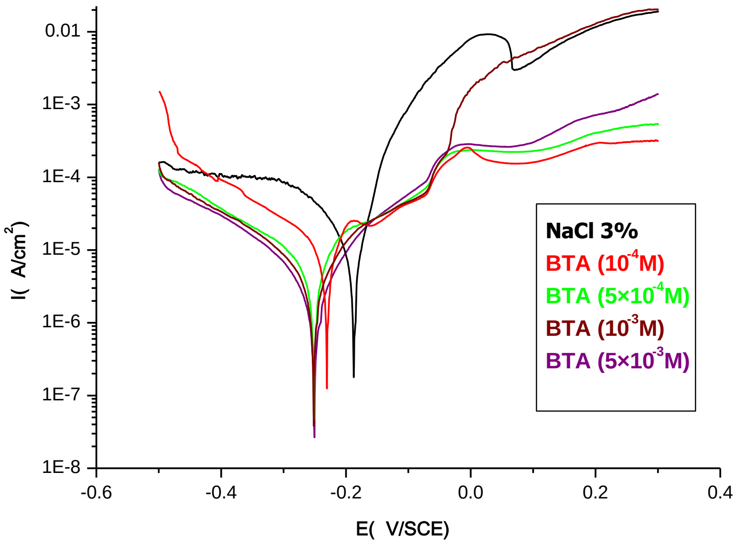

Figure 2: Polarization curves for copper in NaCl 3% at room temperature containing different concentrations of bTA

2.4. SEM examination

SEM images of copper surfaces are shown in Fig. 3. Before immersion, some strips due to the SiC grains of the abrasive paper used during the grinding procedure can be seen (Fig. 3a). After 154h of immersion in 3% NaCl (Fig. 3b) the sample was severely corroded and no protective layer was formed. EDX investigation shows the presence of Cu, Cl, Na and O at the copper electrode surface. In presence of inhibitor, a protective film is observed and only copper and nitrogen were detected by EDX analysis. This is attributed to the ability of bTA molecule to form a protective layer on the copper surface and hence preventing copper pitting and general corrosion (Fig. 3c).

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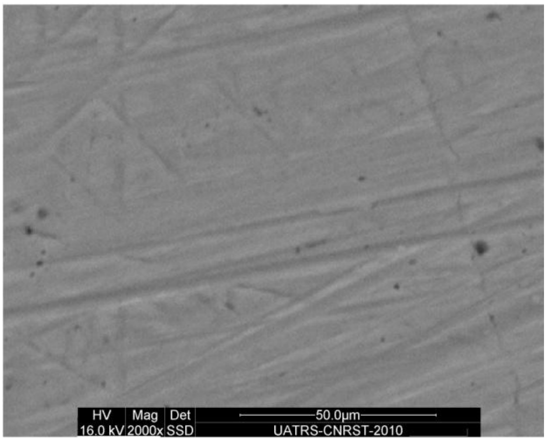
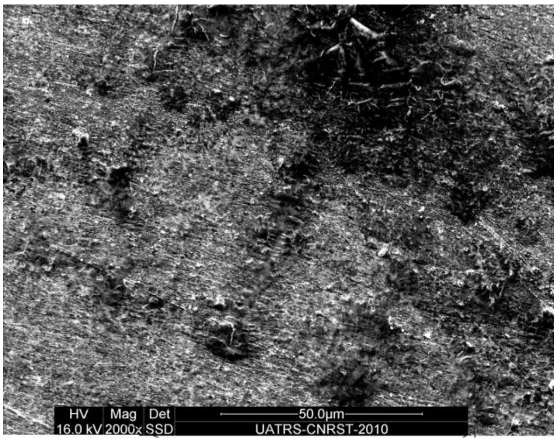
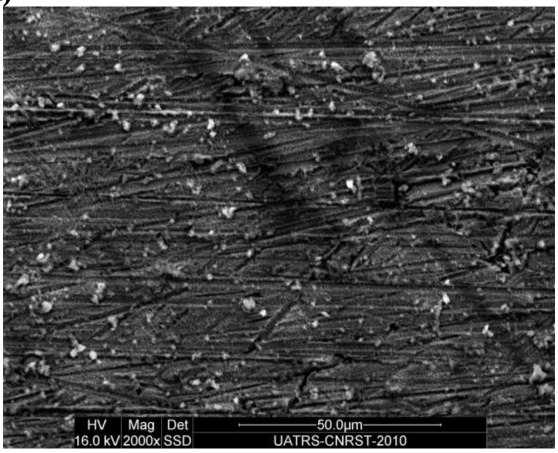


(a)



(b)



(c)

Figure 3: SEM micrographs of the surface of copper before and after immersion in NaCl 3% : (a) before and immersion in a 3% NaCl solution (b) after 154 h of immersion in the absence of inhibitor (c) after 154h of immersion in presence of bTA.

Conclusion

These experimental results clearly show that bTA is an excellent corrosion inhibitor in neutral aqueous sodium chloride solutions, with a high efficiency. The inhibition efficiency was found to increase with inhibitor content to attain 94.63% for 510^{-3}M.

Polarization measurements indicate that bTA acts as a mixed inhibitor, lowering simultaneously the anodic process (dissolution of copper) and the cathodic process (oxygen reduction) and changing the overall mechanism.

In addition, it was shown that the inhibition efficiency of bTA increased with time of immersion and with inhibitor concentration up to 5×10^{-3}M, which is the maximum solubility of the inhibitor in aqueous solution.

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