STUDIA UNIVERSITATIS BABEŞ-BOLYAI, CHEMIA, LI, 1, 2006

STUDY ON THE INHIBITING BEHAVIOR OF A NON-TOXIC THIADIAZOLE DERIVATIVE ON BRONZE CORROSION IN AQUEOUS ELECTROLYTES

IOANA IGNAT[1], SIMONA VARVARA[2] AND LIANA M. MURESAN[1*]

ABSTRACT. The efficiency of a new non-toxic thiadiazole derivative (2 mercapto-5-R-acetylamino-1, 3, 4-thiadiazole) as bronze corrosion inhibitor in various aqueous electrolytes (sodium chloride, sodium sulphate and sodium hydrogen carbonate) was studied by electrochemical polarization measurements. The calculated corrosion parameters suggest that the thiadiazole derivative reduces the rate of bronze corrosion, acting as a mixed-type inhibitor in all the investigated electrolytes. The best inhibiting efficiency of the thiadiazole derivative was observed in sodium chloride solution.

Keywords: bronze corrosion; corrosion inhibitor; thiadiazole derivatives

1. Introduction

Copper and copper-based alloys are widely used in a great variety of applications, such as heat exchangers, building construction, electronics, coinage, art works etc. [1]. In spite of the fact that copper is a relatively noble metal, it corrodes easily in oxygen-containing electrolytes [2]. The corrosion behavior of copper and its alloys in various environments (acidic, alkaline and neutral) has been explored for several decades and, in all cases the dissolution of copper was balanced by the oxygen reduction [3].

Since copper and its alloys are not stable in oxygen-containing electrolytes, substantial improvement in their passivity is needed [4]. To this regard, a range of organic compounds can offer a good protection against corrosion to the exposed copper and bronze surfaces in different aggressive environments. Thus, it is well-known that, on copper and bronze, heterocyclic compounds containing nitrogen, oxygen or sulfur [5-10] are efficient corrosion inhibitors due to the chelating action of heterocyclic molecules and the formation of a physical blocking barrier on the surface [7]. In particular, benzotriazole and its derivatives are among the most effective inhibitors for

[1] "Babes-Bolyai" University, Department of Physical Chemistry, 11 Arany Janos St., 400028 Cluj-Napoca, ROMANIA.
* E-mail: limur@chem.ubbcluj.ro
[2] "1 Decembrie 1918" University, Systemic Archaeology Institute, 11-13 Nicolae Iorga St., 510009 Alba-Iulia, ROMANIA

copper and copper alloys corrosion over a wide temperature and pH range [7, 11-13], but because they are highly toxic [10, 14] they should be replaced with other environmentally friendly inhibitors.

In an attempt to find non-toxic alternatives to the conventional benzotriazole, recent works showed that 2-amino-5-mercapto-1,3,4-thiadiazole is an excellent corrosion inhibitor for copper and bronze in citric acid [15, 16]. In this context, the present work was carried out to investigate the effect of a new thiadiazole derivative, *i.e.* 2 mercapto-5-R-acetylamino-1, 3, 4-thiadiazole on bronze corrosion in different aqueous electrolytes. The efficiency of the inhibitor was studied by electrochemical polarization measurements.

2. Experimental

Materials

Experiments were carried out in different 0.01 M aerated electrolytes (Table 1), at room temperature.

Table 1.
Characteristics of the corrosive media

Electrolyte	NaCl	Na_2SO_4	$NaHCO_3$
pH	5.46	5.76	8.77
λ 10^{-3} (S/cm)	1.243	2.058	1.073

2 mercapto-5-R-acetylamino-1, 3, 4-thiadiazole was synthetized in the laboratories of the Faculty of Pharmacy from Cluj-Napoca, Romania and its molecular structure is presented in figure 1.

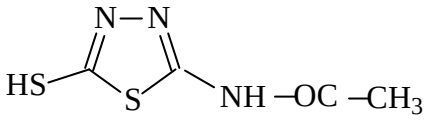

Figure 1.
Molecular structure of the inhibitor

In all the investigated aqueous electrolytes, the concentration range of the inhibitor was 10^{-5} to 10^{-3} M.

All the other chemicals were of analytical grade and used as received.

Methods

Potentiodynamic polarization measurements were conducted using an electrochemical analyzer (Autolab-PGSTAT 10, EcoChemie, Utrecht, Netherlands) connected to a PC for potential control and data acquisition.

Chronopotentiometry was used for the open-circuit potential (O.C.P) measurements.

The electrochemical experiments were performed in a three-electrode cell with a separate compartment for the reference electrode connected with the main compartment *via* a Luggin capillary. The working electrode was made of bronze (see its composition in Table 2), the reference electrode was a saturated calomel electrode (SCE) and the counter electrode was a platinum foil.

Table 2.
Weight % composition of the bronze electrode

Cu	**Sn**	**Pb**	**Zn**	**Sb**	**Ni**	**Fe**	**Mn**	**As**	**S**
87.975	6.014	4.020	1.172	0.299	0.181	0.11	0.002	0.033	0.19
Si	**P**								
0.004	0.004								

Prior to all the polarization runs, the bronze electrode was polished with grit paper of 600, rinsed with distilled water and ethanol, and immersed for 60 minutes in the electrolyte. Anodic and cathodic curves were recorded in a potential range of $E = E_{corr} \pm 200$ mV with a scan rate of 0.25 mV s^{-1}. The rotation speed of the working electrode was fixed at 2000 rpm.

3. Results and Discussion

3.1. Open-Circuit Potential (O.C.P) Measurements

The way in which a metal changes its O.C.P. with time upon immersion in a solution could bring information about the reactions taking place at the metal solution interface. In general, a shift of potential towards positive direction denotes passivation behaviour, whilst a shift in the negative direction signifies activation behaviour.

The open-circuit potentials evolution in time for the bronze electrode, recorded immediately after 60 minutes immersion in different electrolytes are presented in Figure 2.

In the absence of the inhibitor, the O.C.P values for the sulphate and hydrogen carbonate electrolytes gradually increase in the positive direction during the first minutes to reach a stationary state characterized by -0.102 V *vs.* SCE and -0.069 V *vs.* SCE, respectively. This passive behaviour could be most probably attributed to the chemisorption of the dissolved oxygen and its reduction together with possible formation of oxide layers and/or hydroxysulfate or hydroxycarbonate on the surface of the electrode [17].

In the chloride medium, the OCP stabilized very quickly after the immersion at -0.379 V *vs.* SCE. Cuprite (Cu_2O), nantokite (CuCl) and tin species (hydroxides and/or hydroxychlorides) could be produced in this case on the bronze surface [16].

Disregarding the electrolyte composition, more anodic values of the O.C.P. are observed in the presence of thiadiazole derivative. The positive potential shift could be associated with the formation of protective film at the electrode surface. This behaviour suggests that, probably, 2 mercapto-5-R-acetylamino-1, 3, 4-thiadiazole is adsorbed on the bronze surface, acting mainly as an inhibitor for bronze corrosion in all the investigated aqueous media.

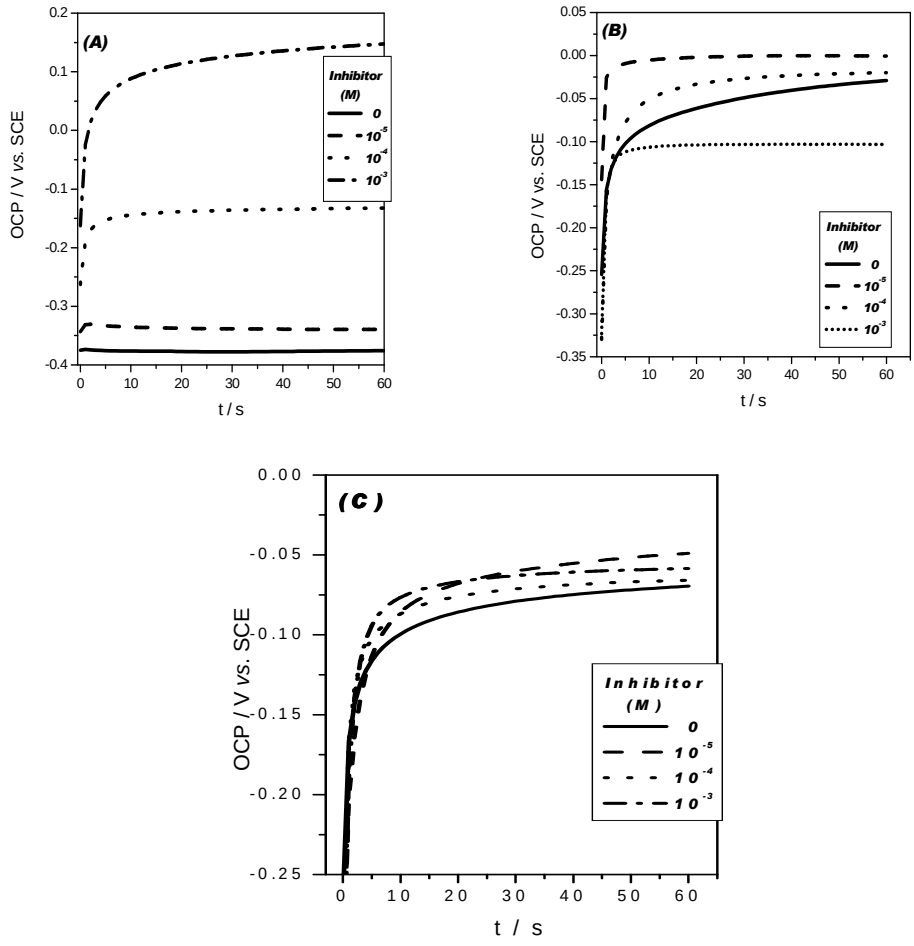

Figure 2.

Open-circuit potentials evolution for the bronze electrode immersed in various 0.01 M aqueous electrolytes without and with different concentrations of 2 mercapto-5-R-acetylamino-1, 3, 4-thiadiazole: (A) NaCl; (B) Na_2SO_4; (C) $NaHCO_3$.

3.2. Potentiodynamic Polarization Measurements

The cathodic and anodic polarization curves of bronze electrodes recorded after its immersion during 60 minutes in different electrolytes in the absence and in the presence of 2 mercapto-5-R-acetylamino-1, 3, 4-thiadiazole are shown in Figure 3.

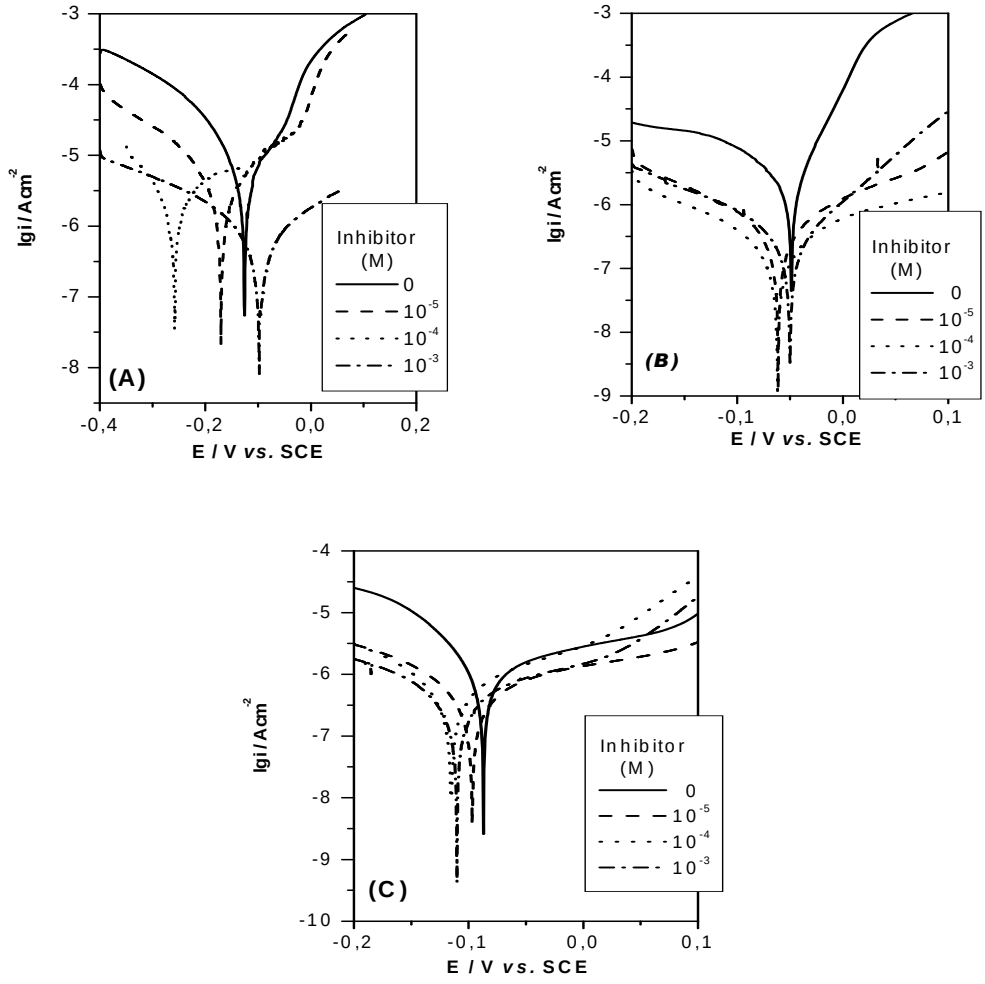

Figure 3.
Influence of thiadiazole derivative concentration on the anodic and cathodic polarization curves of bronze in various aqueous 0.01 M electrolytes: (A) NaCl; (B) Na_2SO_4; (C) $NaHCO_3$.

As can be observed, the anodic curves in NaCl solution are characterized by the presence of a shoulder, which has been attributed to the formation of CuCl on the metal surface [19], according to the reactions [20]:

$$Cu + Cl^- \leftrightarrow CuCl + e^-$$
$$CuCl + Cl^- \leftrightarrow CuCl_2^-$$

It is generally accepted that, in the apparent Tafel region, the corrosion process is controlled by the electrodissolution of copper and the diffusion of soluble $CuCl_2^-$ from outer Helmholtz plane into the bulk solution (mixed control) [21].

Disregarding the electrolyte composition, the addition of the inhibitor determines a considerably decrease both in the anodic and cathodic current density values with respect to the blank solutions. This indicates that the tested thiadiazole derivative cannot be designed exclusively as anodic or cathodic inhibitor. It acts as a mixed-type inhibitor that protects the electrodic surface, and hinders both the anodic dissolution of copper and the cathodic oxygen reduction. However, the slight shift of the corrosion potential values in the negative direction observed in the presence of the inhibitor points to a small predominance of the cathodic reaction.

The corrosion parameters were calculated directly from the potentiodynamic polarization measurements on the basis of the Tafel extrapolation, according to the equation:

$$i = i_0 \exp\left[\frac{2{,}303}{b_a}\left(E - E_{corr}\right)\right] - \exp\left[-\frac{2{,}303}{b_c}\left(E - E_{corr}\right)\right] \quad (1)$$

where b_a and b_c are anodic and cathodic Tafel slopes, $E_{corr\ is}$ the corrosion potential and the other parameters have the usual meaning.

The corrosion inhibition efficiency (IE) in the presence of the inhibitor was calculated from the relation:

$$IE = \frac{i_{corr} - i'_{corr}}{i_{corr}} \cdot 100\,[\%] \quad (2)$$

where i_{corr} and i'_{corr} are the corrosion current densities in the absence and in the presence of the inhibitor, respectively.

The values of the corrosion potential (E_{corr}), corrosion current density (i_{corr}), inhibition efficiency (IE) and of the anodic and cathodic Tafel

slopes (b_a and b_c) for bronze in different electrolytes as a function of the inhibitor concentration are presented in Table 3.

As it can be seen, the corrosion potentials dependence on the inhibitor concentration is not a monotonic one: at very low concentrations (below 10^{-3} M), the inhibitor shifts the corrosion potential slightly to the cathodic direction, while at higher inhibitor concentrations, the corrosion potential shifts to the anodic direction. These variations of the corrosion potential values are probably due to a competition between the anodic and the cathodic inhibiting reactions and/or to the metal surface condition. Moreover, in the presence of 2 mercapto-5-R-acetylamino-1, 3, 4-thiadiazole both the anodic and cathodic Tafel slopes change with the inhibitor concentration, indicating once more that both reactions are influenced by the inhibitor presence.

Relatively high values of the corrosion inhibition efficiency are observed in all solutions. However, it should be noticed that the thiadiazole derivative has a better inhibition effect on bronze corrosion in chloride electrolyte as compared to sulphate or hydrogen carbonate solutions. For chloride and sulphate electrolytes, the optimum concentration for the investigated thiadiazole derivative with the corresponding inhibiting efficiency was 10^{-4} M. In the case of hydrogen carbonate solution, the optimum concentration of inhibitor was 10^{-3} M for an efficiency of around 82 % (table 3).

Table 3.
Corrosion parameters for bronze in different electrolytes in the absence and in the presence of 2 mercapto-5-R-acetylamino-1, 3, 4-thiadiazole at room temperature.

Electrolyte (0.01 M)	**Inhibitor conc.** (M)	**E_{corr}** (mV/SCE)	**i_{corr}** (10^7 Acm^{-2})	**b_c** (V dec^{-1})	**b_a** (V dec^{-1})	**IE** (%)
NaCl	0	-96	41.14	0.115	0.057	-
	10^{-5}	-170	4.28	0.096	0.047	89.60
	10^{-4}	-256	3.43	0.109	0.045	91.66
	10^{-3}	-98	3.72	0.124	0.109	90.95
Na_2SO_4	0	-48	23.30	0.109	0.037	-
	10^{-5}	-60	7.89	0.098	0.049	66.13
	10^{-4}	-62	4.30	0.110	0.032	81.54
	10^{-3}	-50	4.38	0.149	0.077	81.20
$NaHCO_3$	0	-87	7.31	0.122	0.045	-
	10^{-5}	-97	3.02	0.104	0.080	58.68
	10^{-4}	-116	3.53	0.125	0.083	51.71
	10^{-3}	-110	1.31	0.116	0.073	82.08

A possible explanation for the inhibiting action of 2 mercapto-5-R-acetylamino-1, 3, 4-thiadiazole on the bronze corrosion could be found in the covering of the electrodic surface with a protective film made of a polymeric Cu(I)-inhibitor complex. According to [15], the efficiency of the organic inhibitors could be associated to the extent to which they adsorb and cover the metal surface. Their adsorption depends on the structure of inhibitors, on the surface charge of the metal, and on the type of the electrolyte. 2 mercapto-5-R-acetylamino-1, 3, 4-thiadiazole acts as a bidentate ligand both through the aminic and the closed ring nitrogen in the complex.

4. Conclusions

The results of electrochemical investigation show that 2 mercapto-5-R-acetylamino-1, 3, 4-thiadiazole has fairly good inhibiting properties for bronze corrosion in all the investigated electrolytes. It behaves as a mixed-type inhibitor.

The maximum inhibition efficiency of 2 mercapto-5-R-acetylamino-1, 3, 4-thiadiazole was observed in chloride electrolytes. Its inhibiting action can be attributed mainly to the blockage of the bronze surface by a protective film consisting of a polymeric Cu(I)-inhibitor complex in which the inhibitor acts as a bidentate ligand through the aminic nitrogen atom and the closed ring nitrogen.

Acknowledgements

The authors thank Prof. Dr. Robert Sandulescu, from the "Iuliu Hatieganu" University of Medicine and Pharmacy of Cluj-Napoca for supplying us the thiadiazole derivative. The financial support from EGIDE (Project ECO-net No. 10279NA/2005) is gratefully acknowledged.

REFERENCES

1. D-Q. Zhang, L-X. Gao, G-D. Zhou, *J. Appl. Electrochem.*, **2003**, 33, 361–366.
2. M. Pourbaix, "Atlas of Electrochemical Equilibria in Aqueous Solutions"', Pergamon Press, Inc., New-York, 1966.
3. S. Magaino, *Electrochim. Acta*, **1997**, 42, 3, 377-382
4. M. Metikos-Hukovic, R. Babic, I. Paic, *J. Appl. Electrochem.*, **2000**, 30, 617-624.
5. H. Otmacic, E. Stupnisek-Lisac, *Electrochim. Acta*, **2003**, 985-991.
6. R. Tremont, C.R. Cabrera, *J. Appl. Electrochem.*, **2002**, 32, 783–793.
7. H. Ma, S. Chen, L. Niu, S. Zhao, S. Li, D. Li, *J. Appl. Electrochem.*, **2002**, 32, 65–72.
8. J. B. Matos, L. P. Pereira, S. M. L. Agostinho, O. E. Barcia, G. G. O. Cordeiro, E. D' Elia, *J. Electroanal. Chem.*, **2004**, 570, 91–94.
9. S. A. Abd El-Maksoud, *Electrochim. Acta*, **2004**, 49, 4205–4212.
10. E. Stupnisek-Lisac, A. Gazivoda, M. Madzarac, *Electrochim. Acta* **2002**, 47, 4189-4194.

11. G. Quartarone, G. Moretti, T. Bellomi, G. Capobianco, A. Zingales, *Corrosion*, **1998**, 54, 606-618.
12. N. Huynh, S. E. Bottle, T. Notoya, D. P. Schweinsberg, *Corros. Sci*., **2000**, 42, 259-272.
13. J. L. Guinon, J. Garcia-Anton, V. Perez-Herranz, *J. Appl. Electrochem*., **2000**, 30, 379-384.
14. E. Stupnisek -Lisac, N. Galic, R. Gasparac, *Corrosion*, **2000**, 56, 1105-1111.
15. L. Ying, F. Haitao, Z. Yifan, W. Wuji, *J. Mat. Sci.*, **2003**, 38, 407-411.
16. R. B. Faltermeier, *Studies in Conservation,* **1998,** 44, 121-128.
17. N. Souissi, L. Bousselmi, S. Khosrof, E. Triki, *Mat. Corr.*, **2003**, 54, 318–325.
18. M. Pourbaix, *Corros. Sci.*, **1990**, 30, 963-978.
19. M. Itagaki, M. Tagaki, K. Watanabe, *Corros. Sci.,* **1996**, 38, 1109-1125.
20. C. Deslouis, B. Tribollet, G. Mengoli, M. M. Musiani, *J. Appl. Electrochem*., **1988**, 18, 374-393.
21. A. L. Bacarella, J. C. Griess, *J. Electrochem. Soc.,* **1973**, 120, 459-467.