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Dedicated to prof. dr. I. C. Popescu
on the occasion of his 70th anniversary

INHIBITION EFFECT OF SOME THIADIAZOLE DERIVATIVES ON BRONZE CORROSION

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ABSTRACT. The anticorrosive properties of two thiadiazole derivatives, namely 5 amino-1,2,4- thiadiazole (AT) and 2,5 diamino-1,3,4- thiadiazole (DAT) on bronze corrosion in a complex electrolyte at pH=4 has been studied by open-circuit potential, potentiodynamic polarization, and electrochemical impedance spectroscopy measurements. The results of electrochemical investigations showed that both thiadiazole derivatives protect to some extent the bronze surface from corrosion. In the investigated experimental conditions, the highest inhibition efficiencies values were around 71.3 % and 81.6 % in the presence of 1 mM AT and 10 mM DAT, respectively. The inhibition efficiencies of the organic compounds obtained by electrochemical impedance spectroscopy are in agreement with those obtained from polarization technique.

Keywords: *bronze, corrosion, thiadiazole derivatives, electrochemical impedance spectroscopy, polarisation curve*

INTRODUCTION

Bronze is a relatively noble alloy but its corrosion resistance diminishes when the aggressive solution concentration increases.

Organic inhibitors have the ability to form protective films on the surface of the metal that lead to a remarkable decrease in the corrosion rate by slowing down the anodic and/or cathodic processes [1].

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Heterocyclic compounds with polar functional groups and conjugated double bonds [2, 3-5] have been reported as efficient corrosion inhibitors of copper and its alloys, in various media. The inhibition effect of these organic molecules is usually attributed to their adsorption to the metallic surface. Polar functional groups are considered to be the reaction center that stabilizes the adsorption process [6].

Azole derivatives are well-known corrosion inhibitors for copper and its alloys since they contain nitrogen and sulphur atoms which could coordinate Cu(0), Cu(I) or Cu(II) through the lone pair electrons forming copper–azole complexes [7]. These complexes are generally believed to be polymeric in nature and form an adherent protective film on the electrodic surface, which acts as a barrier to aggressive ions from the corrosive solution.

Recently, various thiadiazole derivatives, *i.e.* 2-amino-5-mercapto-1,3,4-thiadiazole [8-10], 2-amino-5-ethylthio-1,3,4-thiadiazole [11,12] 2-amino-5-ethyl-1,3,4-thiadiazole [13], 2-methyl-5-mercapto-1,3,4-thiadiazole [10], 2-acetamino-5-mercapto-1,3,4-thiadiazole [14, 8], 2-mercapto-5-amino-1,3,4 thiadiazole; 2-mercapto-5-acetylamino-1,3,4-thiadiazole; 2-mercapto-5-methyl-1,3,4-thiadiazole and 2-mercapto-5-phenylamino-1,3,4-thiadiazole [15] have been reported as efficient inhibitors for bronze corrosion in different corrosive media.

Since thiadiazole derivatives are innoxious and inexpensive compounds, in the present paper, we continued our early work in the field [15] by investigating the anticorrosive properties of two new thiadiazole derivatives, namely 5 amino-1,2,4- thiadiazole (AT) and 2,5 diamino-1,3,4-thiadiazole (DAT) on bronze corrosion in a complex solution simulating a corrosive acid rain in a polluted urban environment, at pH =4. It should be noted that the above-mentioned organic compounds have never been tested before as corrosion inhibitors for bronze.

In order to evaluate the inhibiting effect of AT and DAT on bronze corrosion, conventional electrochemical techniques, such as open-circuit potential, potentiodynamic polarisation and electrochemical impedance spectroscopy (EIS) were used.

RESULTS AND DISCUSSIONS

Open circuit potential measurements

The evolution of the open-circuit potential (E_{oc}) for bronze over 1 hour immersion in the corrosive solution at pH = 4, in the absence and presence of different concentration of thiadiazole derivatives is illustrated in Figure 1.

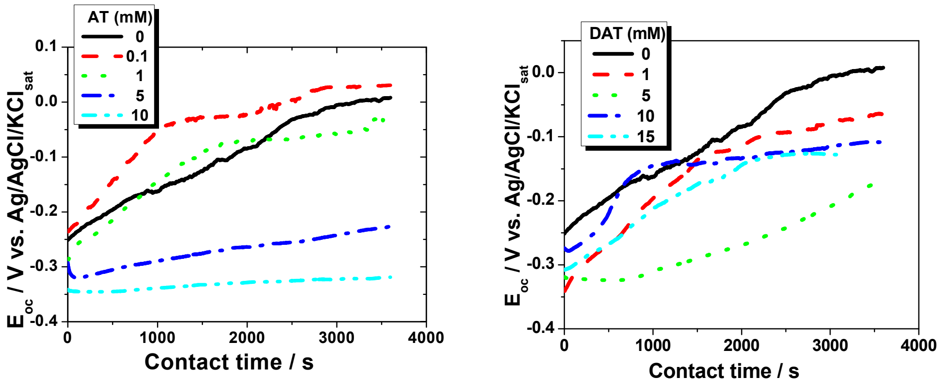


Figure 1. Time-variation of the open-circuit potential for bronze during its immersion in the corrosive media (pH 4), in the absence and in the presence of thiadiazole derivatives at various concentrations.

The values of E_{oc} for bronze corrosion in the presence of different concentrations of AT and DAT are presented in Table 1.

Table 1. Open-circuit values for bronze in the corrosive solution (pH 4) in the absence and in the presence of different concentrations of thiadiazole derivatives

Inhibitor conc. (mM)	**E_{oc} (V*vs.*Ag/AgCl/KCl$_{sat}$)**
0	0.008
AT	
0.1	0.031
1	-0.031
5	-0.227
10	-0.319
DAT	
1	-0.058
5	-0.170
10	-0.108
15	-0.130

The results in Table 1 show that, with the exception of 0.1mM AT, the E_{oc} values in the presence of both investigated thiadiazole derivatives are shifted towards negative values comparing to the value obtained in the inhibitor-free electrolyte, indicating that these organic compounds have stronger effect on oxygen cathodic reduction than on the copper dissolution.

Polarization curves

Fig. 2 presents the cathodic and anodic polarization curves obtained for bronze corrosion in the absence and in the presence of various concentrations of thiadiazole derivatives.

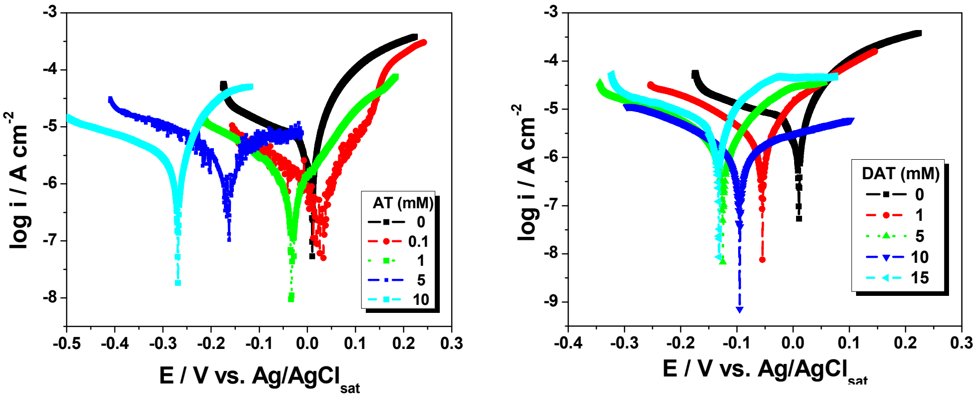


Figure 2. Anodic and cathodic polarization curves for bronze corrosion obtained in the absence and in the presence of different concentrations of AT and DAT in the corrosive solution at pH 4.

The kinetic parameters including the corrosion potential (E_{corr}), corrosion current density (i_{corr}), anodic Tafel slopes (β_a) and cathodic Tafel slopes (β_c) have been determined from the polarization curves by Tafel extrapolation method and their values are presented in Table 2.

The inhibition efficiency (z) values also listed in Table 2 were calculated using the following equation:

$$z = \frac{i^0_{corr} - i_{corr}}{i^0_{corr}} \times 100\,[\%] \qquad (1)$$

where i^0_{corr} and i_{corr} are the values of the corrosion current densities in absence and in presence of thiadiazoles, respectively.

It is noticeable in Figure 2 that the increase in the concentration of thiadiazole derivatives reduces both the cathodic and anodic current densities. Except for the case of 0.1 mM AT, the addition of the two thiadiazole derivatives in the corrosive solution shifts the corrosion potential values to negative direction, as compared to the blank solution, suggesting that AT and DAT inhibits mostly the cathodic process, even though the anodic current densities also decreased. This behavior may be attributed to the adsorption of the organic molecules on the bronze surface through the lone pair of electrons of -N and -S atoms and as a protonated species. As thiadiazole derivatives contain sulphur, they probably self-assemble on the bronze surface forming a protective film. The possible protonation equilibrium of thiadiazole derivatives which may occur in strong acidic media is presented (particularization for DAT) in Figure 3.

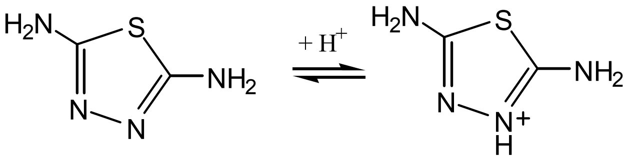


Figure 3. Protonation equilibrium for DAT

Table 2. Kinetic parameters for bronze corrosion in the absence and in the presence of different concentrations of thiadiazole derivatives in the corrosive solution at pH 4.

Inhibitor conc. (mM)	E_{corr} (V*vs.*Ag/AgCl/ KCl_{sat})	i_{corr} ($\mu A/cm^2$)	| β_c | (mV/dec)	β_a (mV/dec)	z (%)
0	-0.102	3.7	242.2	299.8	-
AT					
0.1	0.026	1.4	206.1	80.92	62.2
1	**-0.031**	**1.3**	**176.6**	**117.2**	**64.9**
5	-0.163	2.3	188.8	188.3	37.8
10	-0.279	2.9	213.8	102.1	21.6
DAT					
1	-0.057	1.3	266.9	127.9	64.9
5	-0.124	1.2	173.7	116.2	67.6
10	**-0.089**	**0.8**	**187.6**	**217.1**	**78.4**
15	-0.138	3.2	249.5	123.3	13.5

The changes of the cathodic (β_c) and anodic (β_a) Tafel slopes in the presence of thiadiazole derivatives suggests that the kinetics of both anodic and cathodic processes is affected by the presence of AT and DAT in the corrosive solution, but no definite trend was observed in the shift of (β_c) and (β_a) values.

From Table 2 one can notice that the maximum anticorrosive effectiveness of the thiadiazole derivatives on bronze was attained in the presence of 1 mM AT (64.9%) and 10 mM DAT (78.4%). Nevertheless, in the case of both investigated thiadiazole compounds, a further increase of their concentrations leads to a decrease of the inhibiting efficiency values.

Electrochemical impedance spectroscopy measurements

The Nyquist diagrams of bronze in the corrosive solution in the absence and in the presence of various concentrations of thiadiazole are given in Figure 3. These curves have been obtained after 1 h immersion of the bronze electrode in the corresponding electrolytes.

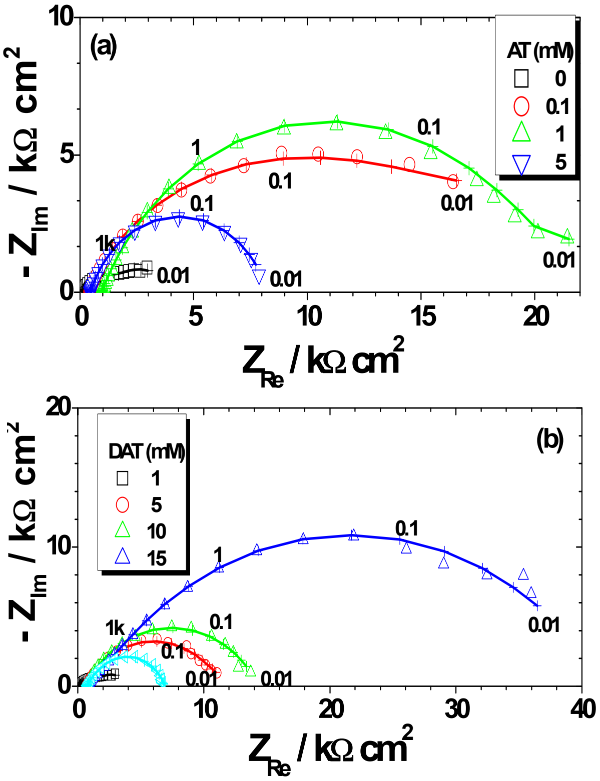


Figure 3. Nyquist plots of bronze electrode in the corrosive solution (pH 4), in the absence and in the presence of different concentrations of AT (a) and DAT (b). The symbol (—+—) corresponds to the simulated spectra. Frequencies are expressed in Hz.

The impedance diagrams exhibit a capacitive behavior with depressed loops in the whole frequency range, both in the absence and in the presence of AT and DAT. The increases of the capacitive loops diameters in the presence of the thiadiazole derivatives as compared to the blank solution is an indicative of the inhibition extent of the bronze corrosion process.

In the impedance diagrams from Figure 3, two capacitive loops could be observed although their separation is not always clear. Consequently, the equivalent circuit used for fitting experimental data is presented in Figure 4.

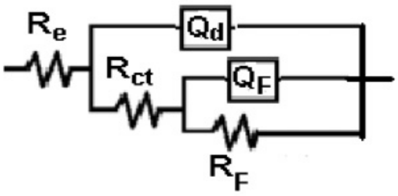


Figure 4. Equivalent electrical circuit used for computer fitting of the experimental data

The high-frequency loop was attributed to the charge transfer resistance and to the double-layer capacitance, while the low frequency loop was associated with the redox process taking place at the electrode surface, most probably involving the corrosion products (*i.e*. Cu(0) and Cu(I)), in accordance with other authors view [16]. In order to get more accurate fit of experimental data, the elements represented in the circuit from Figure 4 as capacitors were actually fitted as constant phase elements (CPEs) represented by the terms, *Q* and *n.* Constant phase elements have already been widely used [17, 18] to account for the deviations brought by the surface roughness of electrode, inhibitor adsorption, the presence of the impurities etc.

The impedance of the CPE is given by the following equation [19]:

$$Q = Z_{CPE(\omega)} = [C(j\omega)^n]^{-1} \qquad (2)$$

where j is an imaginary number and ω is the angular frequency in rad s^{-1}; depending on the value of the exponent n, CPE could be a resistor with the resistance, R ($n = 0$); a capacitor with the capacitance, C ($n = 1$); a Warburg impedance, W ($n = 0.5$) or an inductance, L ($n = -1$).

In order to compare the pseudo-capacitance values for bronze corrosion at various concentrations of thiadiazole derivatives, the values of CPEs were recalculated using the equation:

$$C = [R^{1-n}Q]^{1/n} \qquad (3)$$

Figure 3 demonstrates that the experimental and calculated impedance spectra obtained in the absence and in the presence of thiadiazole derivatives superimpose almost perfectly, confirming the validity of the adopted equivalent circuit. The results obtained for different parameters with respect to the thiadiazole derivatives concentrations are presented in Table 3.

In the absence of the inhibitors, the corrosion process leads to a rough electrodic surface and, consequently, to a high value of the double layer capacitance. The decreases of the C_d values in the presence of both investigated thiadiazole derivatives suggests that these compounds act by adsorption at the metal/solution interface. The charge transfer resistance, R_{ct} increases when AT and DAT are added to the corrosive solution which could be related to the inhibiting proprieties of these compounds on bronze dissolution. This effect is improved upon increasing thiadiazole derivatives concentration up to certain values. For instance, the highest values of R_{ct} were obtained in the presence of 1 mM AT and 10 mM DAT. However, the increases of the thiadiazole derivatives concentration leads to a decrease of the charge transfer resistance values probably due to the deterioration of the adsorbed layer. The decreases of the protective effect at high concentration of inhibitors was already reported in the literature in the case of amino acids [1] and azole compounds [4].

It can also be noticed that the R_F values become greater in the presence of AT and DAT, while the C_F values decrease. Based on these observations it was assumed that the occurrence of the adsorbed inhibitors on the electrodic surface might impede the corrosion products formation. Furthermore, AT and DAT could stabilize the species covering the electrode which became less susceptible to redox processes and hence providing an enhanced protection of the bronze [20].

According to K. Marusic et al. [16], in presence of a redox process taking place at the electrodic surface, the polarization resistance, R_p calculated as the sum of R_{ct} and R_F is the parameter more closely correlated with the corrosion rate. This relationship was demonstrated in the case of bronze corrosion, when an electrochemical reaction following the Tafel law takes place at the electrodic surface, in addition to the charge transfer.

Table 3. Electrochemical parameters of bronze corrosion in the corrosive solution (pH 4) obtained in the absence and in the presence of different concentrations of thiadiazole derivatives

Inhib conc (mM)	**R_e kΩ cm^2**	**R_{ct} kΩ cm^2**	**Q_d μF s^{n-1} cm^{-2}**	**n_d**	**C_d μF cm^{-2}**	**R_F kΩ cm^2**	**Q_F μF s^{n-1} cm^{-2}**	**n_F**	**C_F μF cm^{-2}**	**R_p kΩcm^2**	**z %**
0	0.36	1.4	10.5	0.62	74.9	4.8	1410	0.70	3420	6.2	-
					AT						
0.1	0.40	5.4	50.5	0.73	31.1	10.6	60.8	0.76	42.8	16.0	61.3
1	0.27	7.6	29.1	0.73	16.5	13.9	5.2	0.69	1.6	21.5	**71.3**
5	0.45	2.1	42.3	0.80	23.0	6.7	4.5	0.81	1.9	8.8	29.9
					DAT						
1	0.67	5.7	50.5	0.81	37.7	6.8	50.5	0.81	39.3	12.5	50.6
5	0.72	7.1	36.3	0.77	24.2	7.3	48.9	0.76	35.3	14.4	57.0
10	0.76	9.3	26.34	0.62	11.1	24.2	8.4	0.80	5.7	33.5	**81.6**
15	0.73	2.9	23.3	0.82	12.9	4.1	25.9	0.83	16.4	7.0	11.3

$^{*}R_p = R_{ct} + R_F$

It can be observed from Table 3 that the R_p value increases in the presence of AT and DAT this effect is more pronounced at certain concentrations of thiadiazole derivatives, namely 1 mM AT and 10 mM DAT, respectively.

The inhibition efficiency values, *z* were calculated from the polarisation resistance values, R_p, according to the following equation:

$$z = \frac{R_p - R_p^0}{R_p} \cdot 100 \text{ [\%]} \qquad (4)$$

where R_p and R_p^0 are the polarisation resistances in electrolytes with and without organic compounds, respectively.

In the investigated experimental conditions, the highest inhibition efficiencies values obtained in the presence of the 1 mM AT and 10 mM DAT were 71.3% and 81.6%, respectively.

CONCLUSIONS

In the present paper, open circuit potential, potentiodynamic polarization and electrochemical impedance spectroscopy measurements were used to investigate the anticorrosive effect of two new thiadiazole derivatives, namely, 5 amino-1,2,4- thiadiazole (AT) and 2,5 diamino-1,3,4-thiadiazole (DAT) on bronze in a corrosive solution at pH 4. The results can be summarized as follows:

1. AT and DAT protect to some extent surface of bronze against corrosion and lead to a decreases of the corrosion rate with respect to the blank solution.
2. Potentiodynamic polarization results revealed that both thiadiazole derivatives appears to have a more pronounced inhibiting effect on the oxygen cathodic reduction than on the copper dissolution process, as attested by the significant shift of the corrosion potential towards negative values. However, they causes a decrease of both anodic and cathodic current density values.
3. The (2RC) equivalent-electrical-circuit was successfully used for modeling the bronze/electrolyte interface and the corresponding surface processes, both in the absence and in the presence of thiadiazole derivatives.
4. In the investigated experimental conditions, the highest inhibition efficiencies values were 71.3% and 81.6% in the presence of 1 mM AT and 10 mM DAT, respectively. The inhibition efficiencies of the tested compounds obtained by electrochemical impedance spectroscopy are in agreement with those obtained from polarization technique.

EXPERIMENTAL SECTION

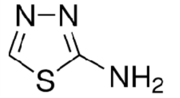
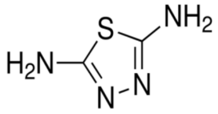
The two thiadiazole derivatives used in this research were synthesized in the laboratory following a procedure previously reported [21].

Chemical formula, molecular mass and molecular structure of the investigated thiadiazole derivatives are presented in Table 4.

All the solutions containing thiadiazole derivatives were prepared using distilled water and ethanol (90:10, v:v) from which appropriate volumes were introduced into the corrosive medium in order to obtain concentrations of 0.1; 1, 5, 10 or 15 mM, depending on the compound's solubility limit.

A complex electrolyte was used as synthetic acid rain at pH 4.The composition of this electrolyte is 31.85 mg/L H_2SO_4 + 46.2 mg/L $(NH_4)_2SO_4$ +31.95 mg/L Na_2SO_4 + 15.75 mg/ L HNO_3 + 21.25 mg/L $NaNO_3$ + 84.85 mg/L NaCl [1]. All solutions were prepared using analytical grade reagents (Merck) and distilled water.

Table 4. Structural and molecular formulas of the investigated thiadiazole derivatives

Thiadiazole (Abbreviation)	**Formula/ Molecular weight (g/mol)**	**Structure**
5 amino-1,2,4- thiadiazole **(AT)**	$C_2H_3N_3S$ M= 101.16	
2,5 diamino-1,3,4- thiadiazole **(DAT)**	$C_2H_4N_4S$ M=116.15	

The working electrode was made of bronze with the chemical composition presented in Table 5.

To avoid the electrolyte infiltration, the working electrode was made of a bronze cylinder rod that was first covered with a cataphoretic paint layer and cured at 150 ^{0}C for 15 min. Then, the bronze cylinder was embedded into an epoxy resin leaving only a circular cross section (0.283 cm^{2}) in contact with the corrosive solution. Prior to use, the bronze surface was mechanically polished using emery paper of 600, 800, 1200, 2400, and 3600 granulation and consecutively rinsed with distilled water. The surface was also polished with Al_2O_3 powder (0.05 μm), and rinsed with distilled water. The last step in preparing the electrode for experiments was immersing it in a 1:1 mixture of distilled water and ethanol and ultrasonicatting it for 10 minutes.

A three-electrode cell was used for the electrochemical experiments. The counter-electrode was a platinum grid and an Ag/AgCl/ KCl_{sat} electrode was used as reference electrode.

Table 5. Chemical composition (% at) of the bronze working electrode

Cu	Sn	Pb	Zn	Ni	Fe	S
94.03	3.31	0.24	1.44	0.25	0.22	0.51

Electrochemical experiments were performed at room temperature, using a a PAR model 2273 potentiostat controlled by a PC computer. Before each experiment, the bronze electrode was left at the open circuit potential for 1 hour in the corrosive solution.

Polarization curves were recorded at constant sweep rate of 10mV/min and scanning range was from - 200 to +200 mV with respect to the open circuit potential.

Electrochemical impedance measurements were carried out at the open-circuit potential after 1 h immersion of the bronze electrode in the corrosive solution. The impedance spectra were acquired in the frequency range 10 kHz to 10 mHz at 5 points per hertz decade with an AC voltage amplitude of ±10 mV.

The impedance data were interpreted based on equivalent electrical circuits, using the ZSimpWin V3.21 software for fitting the experimental data.

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