Dedicated to Professor Luminița Silaghi-Dumitrescu
on the occasion of her 65th anniversary

ELECTROCHEMICAL INVESTIGATION OF THE INHIBITING EFFECT EXERTED BY THE SULFURIC ACID DIAMIDE ON BRONZE CORROSION

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ABSTRACT. The present study is aiming to study the effect of sulfuric acid diamide (SAD) on corrosion of bronze CuSn8. In order to determine the optimal corrosion inhibiting effect SAD was tested at different concentrations. The inhibiting effect of the SAD was investigated by electrochemical methods, in a 0.2 g / L Na_2SO_4 + 0.2 g / L $NaHCO_3$ (pH = 5) solution simulating acid rain. The results show that SAD exerts a good protection in case of CuSn8.

Key words: bronze corrosion, inhibitor, acidic solutions, electrochemical techniques

INTRODUCTION

Because of increasing urban pollution in recent years, bronze statues exposed in these areas are subject to accelerated corrosion, resulting in the destruction of the protective layer formed over time (noble patina). The artistic aspect is also suffering due to the appearance of leaks, discoloration and the crystallization of impurities on the bronze surface.

For bronze protection against corrosion are used various inhibitors, most of them containing S and N in their molecules, such as thiadiazoles [1 - 7], imidazoles [1, 8 - 9], antibacterial drugs [10] etc. It is preferable that they do not modify the noble patina artistic appearance.

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In this context, in order to improve the corrosion resistance of bronze CuSn8 surface, the aim of this paper was to investigate the protective effect of sulfuric acid diamide (**SAD**) at different concentrations on bronze CuSn8 surface, in a solution containing Na_2SO_4 + $NaHCO_3$ (pH5) that simulated an acid rain in urban environment. The protective effect of **SAD** was investigated by electrochemical methods (potentiodynamic polarization measurements and electrochemical impedance spectroscopy).

RESULTS AND DISCUSSION

Open circuit potential measurement

In order to evaluate inhibiting properties of **SAD** at different concentrations, the experiments were started with the open circuit potential (OCP) measurements as a function of time. In Fig. 1 there are shown the OCP evolution for all concentrations of **SAD** studied, as well as in the absence of SAD, in the corrosion solution (pH 5). We can observe that all curves present a similar electrochemical behavior. In time, there is an increase of the values of OCP, but after approximately 15 minutes, it can be observed a regular evolution caused by a stable process at electrode / corrosive solution interface. It can be also observed that in the case of the presence of **SAD** OCP values are more negative than in the case of its absence, suggesting interactions of **SAD** molecules with the cathodic depolarization reaction [4].
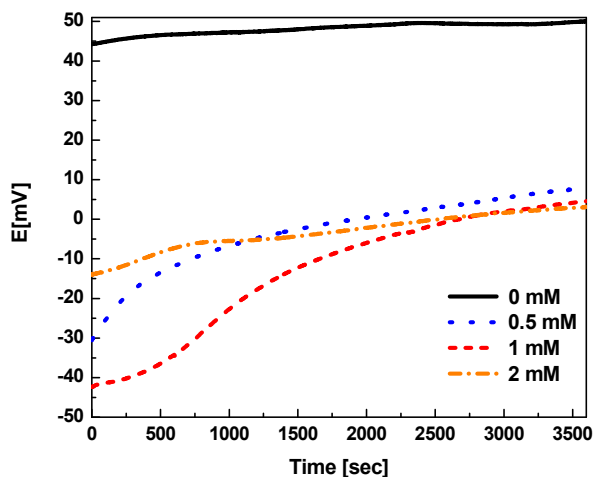

Figure 1. Open circuit potential measurements for the examined samples in absence / presence of **SAD**, immersed in corrosion solution, pH 5

Potentiodynamic polarization measurements

One hour after immersion of bronze electrodes in the corrosive solution in the presence or absence of various **SAD** concentrations (pH 5), the linear polarization curves were recorded at a potential scan rate of 10 mV / min., in the potential domain of ± 20 mV *vs.* the value of the open circuit potential (OCP). The polarization resistance values, R_p^*, calculated as the inverse of the slope of each curve in case of all **SAD** concentrations, are shown in Table 1.

To determine the kinetic parameters of the corrosion process, polarization curves were recorded in the potential range of ± 200 mV *vs.* OCP Fig. 2. The results obtained by Tafel interpretation are also shown in Table 1.

Table 1. Corrosion process parameters for the examined samples
in 0.2 g/L NaSO$_4$ + 0.2 g/L NaHCO$_3$ (pH = 5)

C [mM]	i_{corr}	E_{corr}	β_a	β_c	R_p^*	*IE* [%]	
	[µA/cm^2]	[mV]	[mV]	[mV]	[kΩcm^2]	i_{cor}	R_p^*
0	1.46	41.57	255.55	76.82	9.05	-	-
0.5	0.41	1.52	182.18	203.85	48.30	72	81
1	0.16	-6.65	106.86	313.72	176.00	**89**	**95**
2	0.39	1.14	406.10	168.29	44.85	73	80

Based on the corrosion current density (i_{corr}) the protection efficiencies IE, calculated with the formula (1) are highest when a 1mM solution of **SAD** was used.

$$IE[\%] = \frac{i_{corr}^0 - i_{corr}}{i_{corr}^0} x100 \qquad (1)$$

i^0_{corr} and i_{corr} are the values of the corrosion current densities in absence and in presence of the **SAD** at different concentrations, respectively.

IE was also calculated with the formula (2):

$$IE[\%] = \frac{R_p - R_p^0}{R_p} x100 \qquad (2)$$

R^0_p and R_p are the values of the polarization resistance in absence and in presence of the **SAD** at different concentrations, respectively. The results calculated by equation (2) are in accordance with the previous ones.

As shown in Table 1, the sulfuric diamide exerts a protective effect against bronze corrosion at all investigated concentrations. The best results were noticed at 1 mM *SAD*, this being suggested by the high value of the polarization resistance (R_p=**176.00** [$k\Omega cm^2$]) and the low value of the corrosion current density (i_{corr}= **0.16** [$\mu A/cm^2$]). It can be assumed that the beneficial action of the organic compound is due to S and N heteroatoms from its molecules determining its adsorption on the bronze surface.

This behaviour it can be ascribed to the formation of the uniform and stable passive layer on bronze surface. According to Chiavari the layer of corrosion products formed, prevents especially the oxygen diffusion to the bronze surface [11].

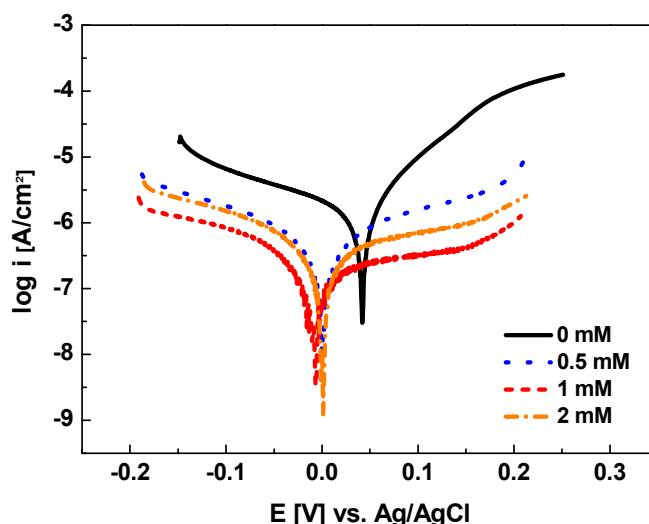Based on these results *SAD* can be considered an efficient corrosion inhibitor for bronze.

Figure 2. Polarization curves (± 200 mV vs. ocp) for the studied electrodes immersed in 0.2 g / L Na_2SO_4 + 0.2 g / L $NaHCO_3$ (pH = 5) at different concentrations of **SAD,** potential scan rate, 10 mV / min.

Electrochemical impedance spectroscopy

The corrosion behaviour of bronze after 1 h immersion in the corrosive solutions without and with various concentrations of *SAD* was more deeply investigated by electrochemical impedance spectroscopy (EIS). The measurements were conducted at 1 hour, 24, 48, respectively 72 hours from the immersion in the corrosive solution and the obtained Nyquist diagrams are presented in Fig. 3.

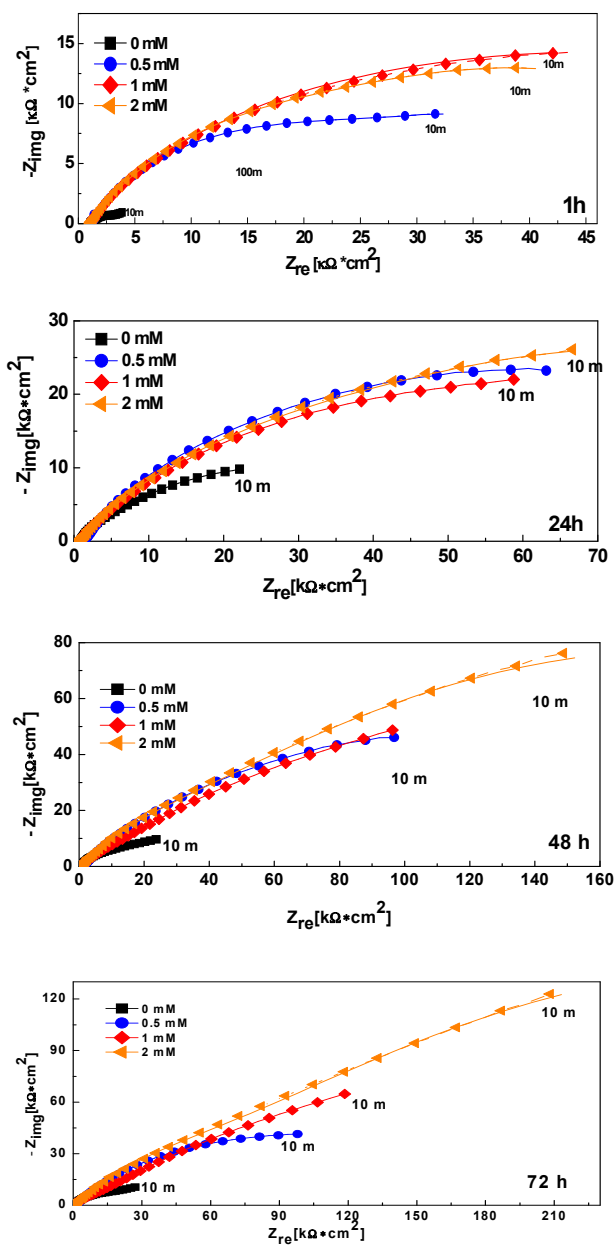**Figure 3.** Nyquist impedance diagrams of bronze electrode in Na_2SO_4 / $NaHCO_3$ (pH 5) solution without / with various concentrations of *SAD* as a function of immersion time; the lines represent fitted data.

It can be noticed that the impedance spectra exhibit a capacitive behaviour in the whole frequencies domain. The experimental impedance spectra were analyzed by fitting to the (2RC) equivalent electrical circuit (Fig. 4), which was previously used to model bronze corrosion in the presence of corrosion inhibitors [10 - 12]. The origin of various variables used in the equivalent circuit from Fig. 4 is as follows: Re: Electrolyte resistance; R_t: Charge transfer resistance; C_d: Double layer capacitance at the bronze | electrolyte interface; R_f: Faradic resistance of the corrosion products accumulated at the interface; C_f: Faradic capacitance due to an oxidation - reduction process taking place at the electrode surface, probable involving the corrosion products, n_d, n_f: Coefficient representing the depressed feature of the capacitive loop in *Nyquist* diagram (n = [0.52 – 0.81]).

The polarization resistance R_p, can be calculated as the sum $R_f + R_t$ [1], and is inversely proportional to corrosion rate. The protective effectiveness of the SAD calculated from R_p values (according to the relation 2), is presented in Table 2.

As can be observed, the used equivalent circuit suitably reproduce the experimental data corresponding to bronze corrosion in the absence and in the presence of **SAD** (Fig. 3). The parameters obtained by non - linear least square fitting and the calculated inhibition efficiencies are given in Table 2. It can also be observed that after 1 hour of immersion, the efficiency is also highest in case of addition of 1mM **SAD** (**92.22** %), thus confirming the results obtained from the polarization curves. Generally, the inhibition efficiencies are higher at short immersion times and are situated around 90 %.

Table 2. Electrochemical parameters of bronze corrosion in Na_2SO_4 / $NaHCO_3$ (pH 5) solution obtained in the absence / the presence of various concentrations of **SAD**.

| C [mM]	Time [h]	R_e [kΩcm²]	R_t [kΩcm²]	C_d [μF/cm²]	R_f [kΩcm²]	C_f [μF/cm²]	R_p [kΩcm²]	IE[%]
0	1	1.03	3.04	321.8	2.12	837	5.16	-
	24	0.937	11.67	48.55	34.58	678.4	46.25	-
	48	0.782	15.99	39.76	39.02	616.2	55.01	-
	72	0.675	18.17	27.48	43.90	608.2	62.07	-
0.5	1	1.22	19	29.58	21.67	301.8	40.67	**87.31**
	24	1.30	67.6	36.15	120.8	644.8	118.98	61.13
	48	0.93	80.4.	35.2	156.3	33.16	192	71.35
	72	0.72	50.09	2.03	135.2	2.8	185.29	66.50
1	1	1.05	47.52	45.96	18.78	602.1	66.3	**92.22**
	24	0.752	49.95	30.40	59.97	222	109.92	57.92
	48	0.295	44.02	20.36	58.5	190.52	102.52	46.34
	72	0.303	36.57	22.73	233.6	10.12	270.17	77.03
2	1	0.97	33.69	26.79	31.35	480.4	65.04	**92.07**
	24	0.63	67.08	27.53	68.46	353.1	135.54	65.88
	48	0.51	85.73	7.1	286	71.99	371.73	85.20
	72	0.54	143.6	6.43	472	65.36	615.6	89.91
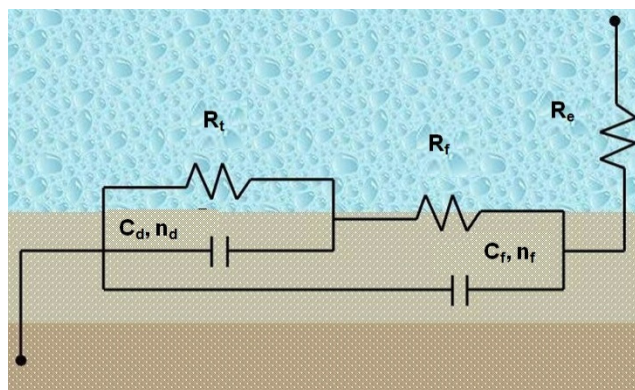
Figure 4. Equivalent electrical circuit used for fitting
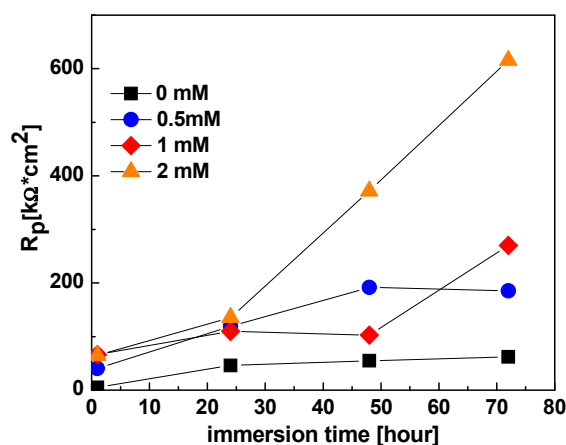of the experimental results (2RC)

Figure 5. Variation of the polarization resistance
in time at different **SAD** concentrations.

The increase in polarization resistance observed in the presence of various concentrations of **SAD** compared to the values obtained in the absence of **SAD** may be associated with the slowing down of corrosion process. It can be observed that the polarisation resistance values are changing during time for all **SAD** concentrations (Fig. 5). A relative stabilization in time is noticed only at 0.5 mM **SAD**, probably due to a stabilization of the corrosion products layer. At high concentrations, R_p increases in time suggesting a thickening of the protective inhibitor film formed on the electrode surface by its adsorption.

CONCLUSIONS

Inhibiting effect of the sulfuric acid diamide at different concentrations on artistic bronze were investigated in Na_2SO_4 / $NaHCO_3$ (pH 5) solution. Electrochemical investigations (polarization and impedance measurements) revealed that sulfuric acid diamide exerts a good protective effect against bronze corrosion in case of all various concentrations. The best anticorrosive effect was noticed after 1 hour of immersion in corrosion media when 1mM inhibitor was used, but after 72 hour immersion the best protection is exerted by 2 mM *SAD*.

The corrosion behaviour of the bronze immersed in Na_2SO_4 / $NaHCO_3$ (pH 5) solution can be simulated with a 2RC electric circuit.

EXPERIMENTAL

Materials

For the working electrodes was used a complex tin bronze alloy that contains a series of secondary alloying elements: 90.18 % copper, 8 % tin, 0.8 % zinc, 1 % lead and 0.02 % aluminium.

The working electrodes were made from a cylindrical bronze rod, placed in a PVC tube and embedded in an epoxy resin, so that only the disc-shaped cross section ($S = 2$ cm^2) of the rod was exposed to the corrosive electrolyte. For electrical contact, a metal rod was attached. It were used four bronze electrodes. Before each electrochemical measurement, the bronze electrode was mechanically polished using successive grades of silicon carbide paper up to grade 2000 to obtain a planar and smooth surface. Finally, the bronze electrodes surface were rinsed with distilled water.

Corrosion inhibitor

The inhibitor used in the experiments was a non - toxic sulfonamide derivative, namely sulfuric acid diamide ($H_2NSO_2NH_2$) (Fig. 6). The inhibitor was dissolved in the corrosive solution at different concentrations respectively: 0.5 mM, 1 mM, 2 mM. The electrolyte solution for corrosion measurements was 0.2 g / L Na_2SO_4 + 0.2 g / L $NaHCO_3$ acidified to pH = 5 by the addition of a dilute sulfuric acid at room temperature.
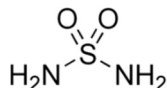

Figure 6. The molecular structure of the inhibitor

Experimental investigation

The electrochemical corrosion measurements were performed on a PC – controlled electrochemical analyzer AUTOLAB - PGSTAT 10 (Eco Chemie BV, Utrecht, The Netherlands) using a three electrodes cell containing a working electrode (bronze), an Ag/AgCl electrode as reference electrode and a platinum counter electrode. Anodic and cathodic polarization curves were recorded in a potential range of ± 20 mV (for R_p determination) and of ± 200 mV *vs.* the value of the open circuit potential (for Tafel interpretation), with a scan rate of 10 mV / min, after 1 hour immersion in the corrosive solution.

Electrochemical impedance spectroscopy measurements (EIS) were carried out at the open circuit potential after 1 h, 24 h, 48 h respectively 72 h immersion of the bronze electrode in the corrosive medium. The impedance spectra were acquired in the frequency range 10 kHz to 10 mHz at 10 points/ 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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