“BABES-BOLYAI“University, Cluj-Napoca

Faculty of Chemistry and Chemical Engineering

Corrosion and Anticorrosion Protection of Bronze Artifacts

PhD DISSERTATION

SUMMARY

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Keywords: bronze, corrosion, inhibitors, amino acids, tiadiazoles, surfactants, antibiotics.

THEORETICAL CONSIDERATIONS

1. Introduction

Copper and its alloys are important materials used in industry, electronics, constructions and art, just to name a few. Bronzes from archaeological artifacts, as well as those used in statues exposed to urban environment, undergo an atmospheric corrosion process that will eventually lead to the formation of corrosion products generally called patina. Because of the increase of pollution in the atmosphere, bronze artifacts or art objects will suffer an increase in the corrosion process the moment they are dug out and exposed to a habitual environment. In order to keep corrosion under control, the most effective way is to use corrosion inhibitors [1].

Organic compounds containing nitrogen, oxygen and sulphur could act as inhibitors for bronze, due to their ability to form protective films on the surface of the metal through different mechanisms as adsorption, chemisorption or polymerization [2- 7].

The most effective organic inhibitors for bronze were proved to be benzotriazole (BTA), and its derivatives. Even though their efficiency covers a wide range of pH and temperatures [4- 9] the high toxicity [9-10], the lack of biodegradability, and the fact that they could affect the color of the patina [11] made the necessity of finding new innoxious organic inhibitors a new and challenging direction in electrochemical research.

A new tendency in anticorrosion protection is finding corrosion inhibitors from the category of medical drugs, amino acids, thiadiazoles and surfactants. Because of their availability on the market, their non toxic impact on humans or environment, their low cost, and their chemical composition, these categories of organic inhibitors seem to represent a promising replacement for the old toxic but efficient anticorrosion inhibitors.

This study opens the doors to finding some of the best corrosion inhibitors for bronze from the above mentioned classes of organic compounds.

The main **objectives** of the present work are:

(i) To evaluate the inhibition properties of some innoxious organic compounds that were not studied before as corrosions inhibitors for bronze belonging to different classes, in an attempt to use them for bronze artifacts protection against corrosion

(ii) To identify for each category of inhibitors the optimal concentration of the compounds, at various pH values and using different corrosive media.

(iii) To study the effect of the immersion time in electrolytes containing the optimum concentration of inhibitors on their corrosion protection efficiency

(iv) To evaluate the interaction of each compound with the metal surface by electrochemical impedance spectroscopy (EIS).

(v) To make some structure-reactivity correlations based on the molecular structure of the inhibitors and their inhibiting efficiency in the process of bronze corrosion

The thesis is organized in seven chapters. The first three chapters present some theoretical aspects related to corrosion of copper and bronze, as well as to the experimental methods that were used in the original part of the thesis. The last three chapters describe the experimental conditions and the main results, that are discussed in detail in order to select the best corrosion inhibitors in different corrosive media, at various pHs. Chapter 7 represents the conclusions for this research.

The methods used for this purpose were corrosion potential (open circuit potential) measurements, potentiodynamic polarization measurements, and electrochemical impedance spectroscopy (EIS) experiments. For surface analysis, scanning electronic microscopy (SEM) was used to obtain images of the surface and provide a physical picture of the morphology of the corroded area. Structure-reactivity correlations were made based on quantum chemical calculations.

EXPERIMENTAL RESEARCH. ORIGINAL CONTRIBIUTIONS

4. State-of-the-art and specific objectives

Copper is a relatively noble metal. In spite of that, 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 due to the slowing down of the anodic or cathodic corrosion processes [13].

As already mentioned, typical corrosion inhibitors for copper and its alloys are heterocyclic compounds containing nitrogen, oxygen or sulphur atoms [3-6, 14-23].

The effectiveness of these organic molecules is based on their ability to form a protective film by several mechanisms (*i.e*. adsorption, polymerization etc.) [24-29].

The purpose of this research is to find and test different types of nontoxic compounds such as amino acids, surfactants, thiadiazoles, and antibiotics that were not studied before as corrosions inhibitors for bronze. The corrosive media was also modified from low basic to acidic, in order to simulate soil conditions, acid or neutral rain.

5. Experimental conditions

5.1. Reagents and materials

5.1.1. Inhibitors

In this research four classes of inhibitors were used: amino acids, surfactants, **Aminoacizii**

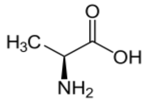
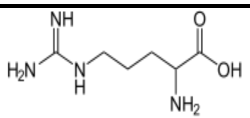
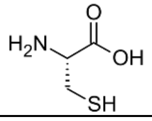
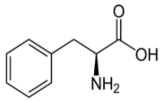
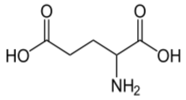
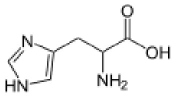
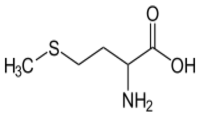
thiadiazoles and antibiotics. The latter were tested only for aluminum and steel protection [16-19]. All of these four classes of compounds have several things in common:

1. they are organic compounds containing either sulphur, nitrogen and/ or oxygen
2. they are non toxic for the environment
3. they are cost effective

A. Amino acids

The seven tested amino acids, produced by Sigma Aldrich, UK, (> 99% purity) used in the first step of this research (the screening step) are presented in Table 5.1.

Table 5.1. Molecular and structural formulas for the tested amino acids.

No.	Amino Acid (Abbreviation)	Formula/ Molecular weight (g/mol)	Structure
1.	**Alanine** *(Ala)*	$C_3H_7NO_2$ *M= 89.09*	
2.	**Arginine** *(Arg)*	$C_6H_{14}N_4O_2$ *M= 174.20*	
3.	**Cysteine** *(Cys)*	$C_3H_7NO_2S$ *M= 121.16*	
4.	**Phenylalanine** *(PhAla)*	$C_9H_{11}NO_2$ *M= 165.19*	
5.	**Glutamic acid** (*Glu*)	$C_5H_9NO_4$ *M= 147.13*	
6.	**Histidine** *(His)*	$C_6H_9N_3O_2$ *M= 155.15*	
7.	**Methionine** *(Met)*	$C_5H_{11}NO_2S$ *M= 149.21*	

After the preliminary screening, we focused our attention only on cysteine, alanine and phenylalanine as corrosion inhibitors for bronze since the results were promising in these cases.

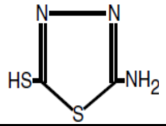
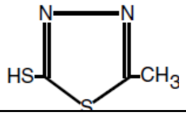
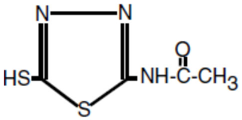
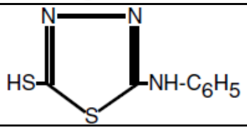
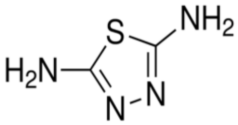
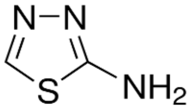
B. Thiadiazoles

Thiadiazoles are innoxious organic heterocyclic compounds that contain nitrogen and sulphur and showed to have inhibiting capabilities for the corrosion of copper or bronze in different corrosive media [14, 30, 31, 32].

The thiadiazole derivatives used in this research were synthesized in the laboratory following a procedure previously reported [33].

The six thiadiazole derivatives investigated are presented in Table 5.2.

Table 5.2. Structural and molecular formulas of the investigated thiadiazoles.

No.	**Thiadiazole (Abbreviation)**	**Formula/ Molecular weight (g/mol)**	**Structure**
1.	**2 mercapto 5 amino 1,3,4 thiadiazole** *(MAT)*	$C_2H_3N_3S_2$ *M= 133.19*	
2.	**2 mercapto 5 methyl 1,3,4 thiadiazole** *(MMeT)*	$C_3H_4N_2S_2$ *M= 132.20*	
3.	**2 acetyl amino 5 mercapto 1,3,4 thiadiazole** *(AcAMT)*	$C_4H_5N_3OS_2$ *M= 175.23*	
4.	**2 phenilamino 5 mercapto 1,3,4 thiadiazole** *(PhAMT)*	$C_8H_7\ N_3\ S_2$ *M= 209.29*	
5.	**2,5 diamino-1,3,4- thiadiazole** *(DAT)*	$C_2H_4N_4S$ *M=116.15*	
6.	**5 amino-1,2,4- thiadiazole** *(AT)*	$C_2H_3N_3S$ *M= 101.16*	

C. Antibiotics

The use of antibiotics as corrosion inhibitors for bronze has not been reported until now, and represents a new development in the quest for finding environmentally friendly compounds as inhibitors.

The six antibiotics used in the attempt to find the best compound at the optimum concentration that can act as corrosion inhibitor for bronze are presented in Table 5.3.

The antibiotics were purchased from mainstream pharmacies and the amount of antibiotic per capsule was 100 mg/capsule for Doxy, 250 mg/capsule for Tetra, 500 mg/capsule (for *Amoxi, Cefadroxil* and *Cipro*) and 1000 mg/capsule for *Strepto*.

D. Surfactants

One of the trends in the studies of corrosion inhibitors for copper is the addition of high molecular weight organic compounds like surface active agents to acidic solution. Ionic and non-ionic surfactants have been reported as corrosion inhibitors for copper and mild steel [34-39]. Research shows that anionic surfactant Sodium Dodecyl Sulfate (SDS) protects the surface of copper better than the cationic surfactant Cetyl Trimethyl Ammonium Bromide (CTAB) [40].

This study focused on the use of two surfactants (Cetyl Trimethyl Ammonium Bromide and Sodium Dodecyl Sulfate) as corrosion inhibitors for bronze in a corrosive media at two pH values. Both surfactants used were analytical grade reagents Merck (Table 5.4)**.**

Table 5.3. Chemical and structural formulas of the antibiotics tested as corrosion inhibitors.

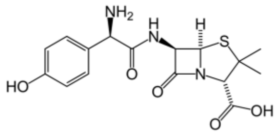
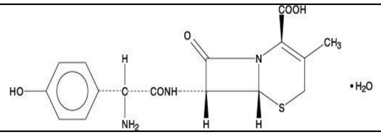
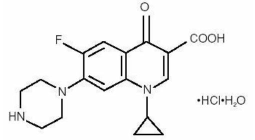
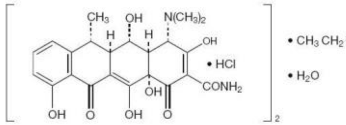
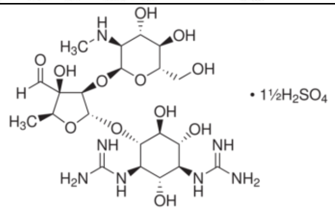
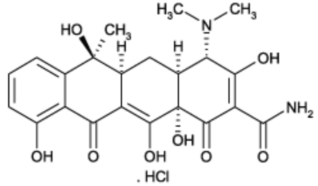
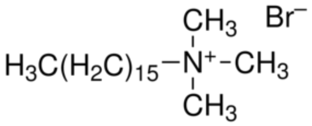
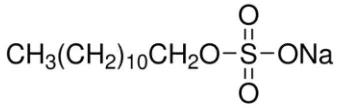
No.	Antibiotic (Abbreviation)	Formula/ Molecular weight (g/mol)	Structure	Commercial name (Manufacturer)
1.	**Amoxicillin trihydrate/** *(Amoxi)*	$C_{16}H_{19}N_3O_5S{\bullet}3H_2O$ *M = 419*		**A**moxicilin trihidrat (Antibiotice SA Iasi)
2.	**Cefadroxil monohydrate** *(Cefadroxil)*	$C_{16}H_{17}N3O_5S{\bullet}H_2O$ *M= 381.40*		Cefadroxil monohidrat (Sandoz)
3.	**Ciprofloxacin hydrochloride** *(Cipro)*	$C_{17}H_{18}FN_3O_3{\bullet}HCl{\bullet}H_2O$ *M =385*		Ciprozone (Ozone Laboratories)
4.	**Doxycycline hyclate** *(Doxy)*	$(C_{22}H_{24}N_2O_8{\bullet}HCl)_2{\bullet}C_2H_6O{\bullet}H_2O$ *M = 952.86*		Doxiciclina hiclat (Europharm)
5.	**Streptomycin sulphate** *(Strepto)*	$(C_{21}H_{39}N_7O_{12})_2{\bullet}3H_2SO_4$ *M =1457.14*		Strevital (Antibiotice SA Iasi)
6.	**Tetracycline hydrochloride** *(Tetra)*	$C_{22}H_{24}N_20_8$ •HCI *M= 480.92*		Tetraciclina (Antibiotice SA Iasi)

Table 5.4. Surfactants: chemical and structural formulas.

No.	Surfactant (Abbreviation)	Formula/ Molecular weight (g/ mol)	Structure
1.	Cetyl Trimethyl Ammonium Bromide *(CTAB)*	$C_{19}H_{42}BrN$ *M= 364.45*	 $H_3C(H_2C)_{15}-\overset{CH_3}{\underset{CH_3}{N^+}}-CH_3\ Br^-$
2.	Sodium Dodecyl Sulfate *(SDS)*	$C_{12}H_{25}O_4S \bullet Na$ *M= 288.37*	 $CH_3(CH_2)_{10}CH_2O-\overset{O}{\underset{O}{S}}-ONa$

5.1.2. Solutions

5.1.2.1. Corrosive electrolyte solutions

Several studies refer to the deterioration mechanisms of copper and bronzes under various climatic conditions, both natural and artificial [40-41].

The purpose of this research was to use corrosive media that mimic the environments that normally bronze is subject to. The following types were chosen:

1. **Electrolyte simulating acid rain:** the corrosive medium was an aqueous aerated solution of **0.2 g/ L Na_2SO_4 + 0.2 g/L $NaHCO_3$, acidified to pH 5 or 3** (for more aggressive corrosion conditions) by addition of dilute H_2SO_4, **or to pH 8** by addition of diluted NaOH. The solutions were prepared using analytical grade reagents (Merck, Darmstadt, Germany) and ion-exchanged water.
2. **Electrolyte simulating rain in a polluted urban environment**: A more complex electrolyte was used as synthetic acid rain at **pH 4**, as neutral rain at **pH** 7 or as alkaline rain at **pH 9**. 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**. [13]. The pH was adjusted with diluted NaOH, and the solutions were prepared using analytical grade reagents (Merck) and distilled water.
3. **Electrolyte simulating soil**: a solution that replicates the corrosive environment of soil, since a lot of the bronze artifacts were buried for very long periods of

time. The composition of this corrosive medium is **0.02 M NaCl + 0.125 M Na_2SO_4 at pH 8** The pH was adjusted with diluted NaOH, and the solutions were prepared using analytical grade reagents (Merck) and distilled water.

5.1.2.2. Inhibitors solutions

1. Amino acids solutions

The amino acids (Sigma Aldrich, UK) used in this research were dissolved in different electrolyte solutions with the concentrations ranging from 10^{-3} mM to 10 mM, depending on the compounds' solubility limit.

Table 5.5 below represents an overview of amino acids solutions in different corrosive media. For comparison the corrosion tests were performed using as corrosion inhibitor 1mM solution of benzotriazole (BTA) (Merck).

Table 5.5. Amino acids: different concentrations in various corrosive media, at different pH values.

No.	Inhibitor: Amino Acids	Concentration (mM)	pH	Corrosive solution
1	Alanine Arginine Cysteine Phenylalanine Glutamic acid Histidine Methionine	1	8	0.02 M NaCl + 0.125 M Na_2SO_4
2	Alanine Cysteine Phenylalanine	0.01 0.1 1 10	3 8	0.2 M Na_2SO_4 + 0.2 M $NaHCO_3$
3	Cysteine	10^{-3} 10^{-2} 10^{-1} 1	4	31.85 mgL^{-1} H2SO_4 + 46.2 mgL^{-1} $(NH_4)_2SO_4$ + 31.95 mgL^{-1} Na_2SO_4 + 15.75 mgL^{-1} HNO_3 + 21.25 mgL^{-1} $NaNO_3$ + 84.85 mgL^{-1} NaCl

2. Thiadiazole solutions

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, 15 or 20 mM, depending on the organic compound’s solubility limit. It should be mentioned that the compounds containing an acetyl amino- (MAcAT) or a phenyl amino-(MPhAT) group present a low solubility in water and their highest concentrations in the electrolyte were 1 mM. The maximum concentrations of MAT and MMeT in the corrosive solution were 5 mM [7].

Table 5.6 below represents the screening of different thiadiazoles solutions.

Table 5.6: Thiadiazoles: concentrations, and pH values.

No.	Inhibitor: Thiadiazoles	Conc. (mM)	pH	Corrosive solution
1	2 mercapto 5 amino 1,3,4 thiadiazoles (MAT) 2 mercapto 5 methyl 1,3,4 thiadiazoles (MMeT) 2 acetyl amino 5 mercapto 1,3,4 thiadiazoles (AcAMT) 2 phenilamino 5 mercapto 1,3,4 Thiadiazoles (PhAMT)	0.1 1 5 10	8	0.02 M NaCl + 0.125 M Na_2SO_4
2	2,5 diamino-1,3,4-thiadiazole (DAT)	1 5 10 15 20	4 7	31.85 mgL^{-1} $H2SO_4$ + 46.2 mgL^{-1} $(NH_4)_2SO_4$ + 31.95 mgL^{-1}Na_2SO_4 + 15.75 mgL^{-1}HNO_3 + 21.25 mgL^{-1}$NaNO_3$ + 84.85 mgL^{-1}NaCl
	5 amino-1,2,4- thiadiazole (AT)	0.1 1 5 10	4 7	

3. Antibiotics solutions

All antibiotics used in this research were dissolved in the electrolyte solution and the concentration ranges were from 50 ppm to 3000 ppm, depending on the compound’s solubility limit. The Table 5.7. below summarizes the types of antibiotics used, their concentrations, solution's pH, and the corrosive electrolyte.

Table 5.7: Antibiotics solutions: concentrations, pH and electrolyte used.

No.	Inhibitor: Antibiotics	Concentration (ppm)	pH	Corrosive solution
1.	Amoxicillin	200 400 600 800 1000	4 7	31.85 mgL^{-1} H2SO$_4$ + 46.2 mgL^{-1} (NH$_4$)$_2$SO$_4$ + 31.95 mgL^{-1}Na$_2$SO$_4$ + 15.75 mgL^{-1}HNO$_3$ + 21.25 mgL^{-1}NaNO$_3$ + 84.85 mgL^{-1}NaCl
2.	Cefadroxil	200 400 600 800	4	
3.	Ciprofloxacin	200 400 600 800 1000 2000 3000	4 7 9	
4.	Doxycycline	100 200 300 400	4 7 9	
5.	Streptomycin	50 100 200 300 400 500	4 7 9	
6.	Tetracycline	200 300 400 500	4 7 9	

3. Surfactants solutions

All surfactants solutions were made by dissolving the appropriate amount of compound in the electrolyte solution. Table 5.8. below summarizes the types of surfactants used in this research, their concentrations, pH, and the corrosive solution.

Table 5.8: Surfactants solutions: concentrations, pH and electrolyte used.

No.	Surfactants	Concentration	pH	Corrosive solution
1	Cetyl Trimethyl Ammonium Bromide (CTAB)	10^{-3} mM 10^{-2} mM 10^{-1} mM 1 mM 10 mM	4	31.85 mgL^{-1} $H2SO_4$ + 46.2 mgL^{-1} $(NH_4)_2SO_4$ + 31.95 mgL^{-1}Na_2SO_4 + 15.75 mgL^{-1}HNO_3 + 21.25 mgL^{-1}$NaNO_3$ + 84.85 mgL^{-1}NaCl
2	Sodium dodecyl sulfate (SDS)	1000 ppm 1500 ppm 2000 ppm 2500 ppm 3000 ppm 4000 ppm	4	

5.1.3. Working electrodes

The working electrodes were made of bronze with the chemical composition presented in the Table 5.9. To avoid the electrolyte infiltration, the working electrode was made of a bronze cylinder rod which was first covered with a cataphoretic paint layer (PGG; W742 and P962), 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 (0.2826 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 50%- 50% mixture of distilled water and ethanol and ultrasonicatting it for 10 minutes.

Tabelul 5.9: Compozitia chimica (%) a electrodului de bronz.

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

5.2 Experimental methods and instrumentation

The electrochemical behavior of bronze in the absence and in the presence of different concentrations of inhibitors was studied by open-circuit potential (OCP) measurements, electrochemical impedance spectroscopy (EIS) and polarization curves (PC).

A three-electrode cell was used for the electrochemical experiments. The counter-electrode was a platinum grid and a Ag/ AgCl/ KCl $_{sat}$ electrode or a saturated calomel electrode (SCE) were used as reference electrodes.

Electrochemical measurements (OCP, PC, EIS) were performed using a PAR model 2273 potentiostat (made in USA).

A scanning electron microscope (SEM) was used for surface analysis.

5.2.1. Open Circuit Potential

Prior to any electrochemical measurement, the electrode and the electrolyte/corrosive solution were in contact for 3600 seconds in order for the system to stabilize, and the open circuit potential E_{oc} was measured.

5.2.2. Polarization curves

For determining the polarization resistance values, Rp, the initial potential was fixed at a value with 20 mV more negative than the open-circuit potential value and then scanned towards more positive values, at the rate of 0.166 mV/ s until a value with 20 mV more positive than E_{oc} was reached.

In order to obtain the Tafel parameters, polarization curves were plotted at a potential range of +/ - 200 mV *versus* E_{oc}.

5.2.3. Electrochemical impedance spectroscopy (EIS)

Electrochemical impedance measurements were carried out at the open-circuit potential after 1 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 per hertz decade with an AC voltage amplitude of ±10 mV. The impedance data were then analyzed with a software based on a Simplex parameter regression.

5.2.4. Scanning Electronic Microscopy (SEM)

For morphological studies, the bronze surface was prepared by keeping the electrodes for 72 hours in electrolytes containing different concentrations of inhibitors. Then, the specimens were washed gently with water, carefully dried and observed without any further treatment, by scanning electron microscopy using a Zeiss Ultra 55 SEM FEG instrument.

6. Results and discucion

6.1. The influence of inhibitors on bronze corrosion

6.1.1. Amino acids

6.1.1.2. Amino acids screening

In order to select the most efficient inhibitors, the first step was to run a series of OCP and EIS testing on a series of six amino acids, at the same concentration of 1 mM and in the same corrosive environment: 0.02 M NaCl and 0.125 M Na_2SO_4 at pH 8, simulating the corrosive environment in soil. The amino acids tested are Cysteine (Cys), Alanine (Ala), Phenylalanine (PhAla), Methionine (Met), Arginine (Arg), Histidine (His), and Glutamic acid (Glu). All the test were done for comparison also on a blank sample, meaning just the bronze electrode immersed in the electrolyte solution, and also, on a 1 mM solution of benzotriazole (BTA) in the same electrolyte. BTA was proven to be the best inhibitor for bronze, and comparing our results with the results obtained by using BTA was necessary to evaluate the effectiveness of these amino acids as corrosion inhibitors.

6.1.1.3. Influence of the inhibitors concentration

A. Bronze corrosion in solutions of different amino acids in a corrosive medium imitating acid rain (pH 3)

Electrochemical impedance spectroscopy measurements

Masuratorile de impedanta au fost efectuate la potentialul de circuit deschis dupa o ora de imersie a electrodului in solutia de electrolit care continea diverse concentratii de aminoacizi. Graficele Nyquist obtinute sunt prezentate in Figura 6.4. Insertiile in figura reprezinta domeniile de impedanta de frecvente mari la o scara marita pentru o mai buna vizibilitate.

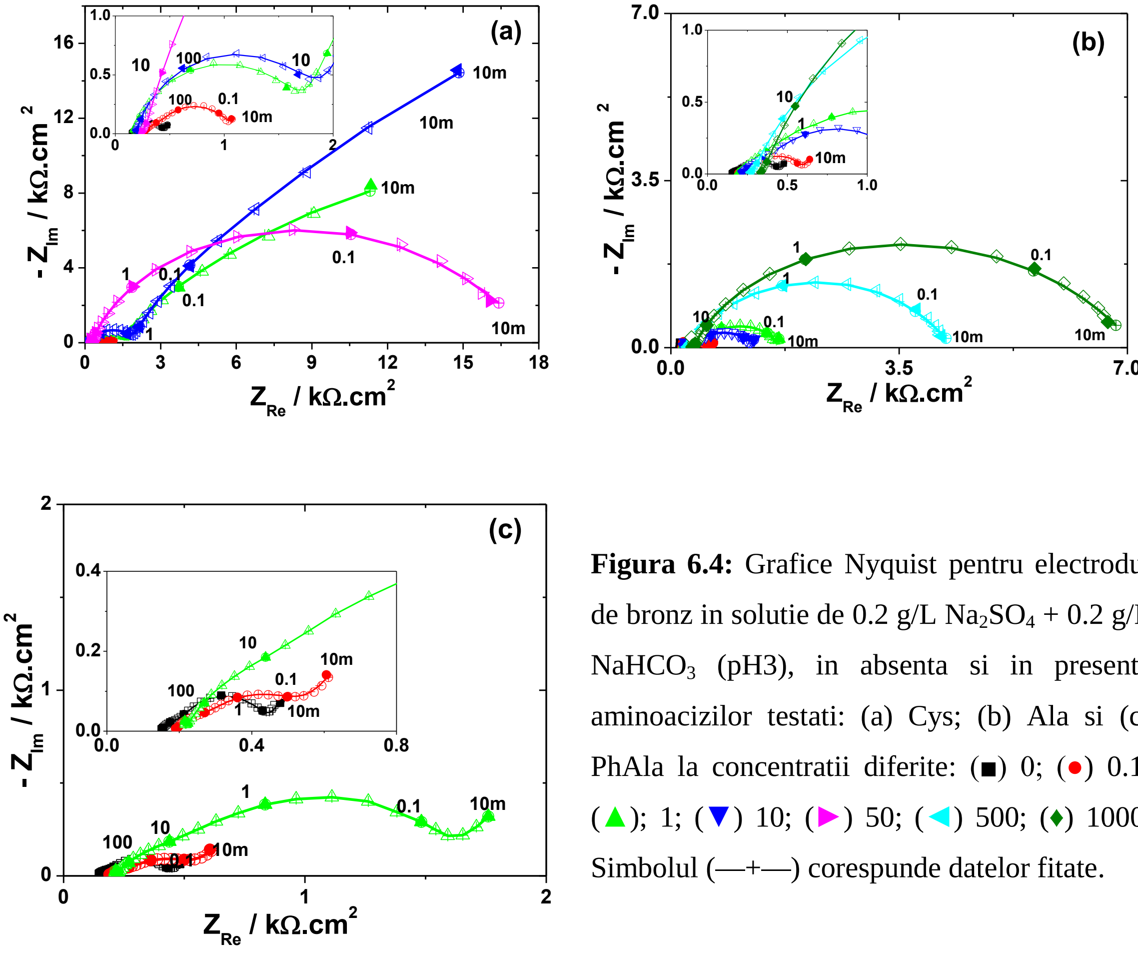


Figura 6.4: Grafice Nyquist pentru electrodul de bronz in solutie de 0.2 g/L Na_2SO_4 + 0.2 g/L $NaHCO_3$ (pH3), in absenta si in presenta aminoacizilor testati: (a) Cys; (b) Ala si (c) PhAla la concentratii diferite: (■) 0; (●) 0.1; (▲); 1; (▼) 10; (▶) 50; (◀) 500; (♦) 1000. Simbolul (—+—) corespunde datelor fitate.

It can be noticed that the impedance spectra of bronze recorded in the absence and in the presence of low concentrations of amino acids (0.1 - 10 mM) show two capacitive loops followed by the beginning of a third capacitive branch in the lowest frequency range. At higher concentrations of Ala and Cys the impedance spectra may be split in three capacitive loops though not clearly separated.

Three capacitive loops are necessary for computer fitting of experimental data obtained in the absence and in the presence of amino acids with an electrical equivalent circuit. The (3RC) electrical circuit presented in Figure 6.5. This circuit was formerly used to explain the copper corrosion in chloride solution of different pH values [42].

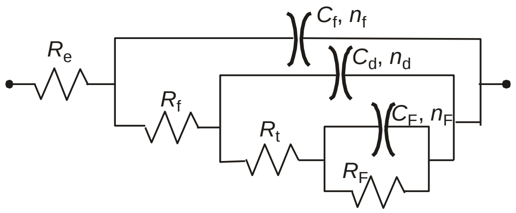


Figure 6.5: (3RC) equivalent electrical circuit used for computer fitting of the experimental data

The (R-C) couples used in the equivalent circuit from Figure 6.5 could be ascribed to the following contributions:

- The high frequency elements (R_f - C_f) are related to the dielectric character of the corrosion products (C_f) due to formation of a thin surface layer (oxide and/or oxide with adsorbed inhibitor) that is reinforced by the presence of the inhibitor and by the ionic conduction through the pores of the film (R_f);

- The medium frequency contribution (R_t - C_d) is attributed to the double layer capacitance (C_d) at the bronze/electrolyte interface at the bottom of the pores coupled with the charge transfer resistance (R_t);

- The low frequency elements (R_F - C_F) are ascribed to the redox process taking place at the electrode surface, probable involving the corrosion products layers accumulated at the interface;

- R_e represents the electrolyte's resistance;

- n_d, n_f, and n_F are coefficients representing the depressed characteristic of the capacitive loops in the Nyquist diagrams.

A capacitive loop is calculated, at the given angular frequency ω (rad s^{-1}) according to the following equation:

$$Z = \frac{R}{1+\left(j\cdot\omega\cdot R\cdot C\right)^n} \qquad \text{where} \qquad 0 < n \le 1 \qquad \text{Eq. 6. 3.}$$

The results of non-linear regression calculation with Simplex method (cross symbols) are superimposed to the experimental data in Figure 6.5 and the obtained impedance parameters are given in Table 6.4.

The good agreement between the experimental and calculated values of the impedance from Figure 6.5 indicates that (3RC) equivalent electrical circuit reproduce properly the experimental data corresponding to the bronze corrosion in strong acidic solution, in the absence and in the presence of the amino acids, respectively.

Comparing the impedance parameters calculated in the presence of the organic compounds with those determined in uninhibited solution (Table 6.4), results that the film resistance R_f generally increases in the presence of the inhibitors, while the film capacitance decreases. These effects are enhanced by increasing the amino acids concentration. This suggests that the surface layer covering the electrode surface in presence of the amino acids is probably thicker and more protective, which makes the ionic conduction through this layer more difficult [42].

The decrease of the C_d values, which results from a decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer, suggests that the investigated amino acids act by adsorption on the metal/solution interface. The charge transfer resistance R_t increases when the organic inhibitors are added to the corrosive solution, indicating a marked anticorrosion effect of the amino acids on bronze dissolution in strong acidic solution.

The value of C_F is compatible with the hypothesis on the origin of this loop attributed to an oxidation–reduction process involving corrosion products. In presence of the amino acids, R_F increases, indicating that these compounds stabilize a species covering the electrode surface [5].

Taking into consideration that the polarization resistance R_p, calculated as the sum $R_f + R_t + R_F$ from the resistance values determined by the regression calculation, is the parameter most closely associated to corrosion rate, the protective effectiveness of the investigated compounds will be assessed by R_p values [43].

The inhibiting efficiency (IE), also presented in Table 6.4., was calculated using the values of the polarization resistance according to the following equation:

$$\text{IE}\ (\%) = \left(\frac{Rp^0 - R_p}{Rp^0} x100 \right) \qquad \text{Eq. 6.4.}$$

where R_p and R_p^0 - are the polarization resistances in electrolytes with and without inhibitors, respectively.

Table 6.4 presents that in most cases, the corrosion rate decreases in the presence of investigated amino acids and this effect is more pronounced at the highest concentration of inhibitors.

In strong acidic solution, the maximum inhibition efficiency values were obtained in the presence of the optimum concentration of amino acids: 10 mM Cys, 1 M Ala and 10 mM PhAla. The inhibition efficiencies of investigated compounds calculated by EIS method show the same trend as those estimated from the polarization measurements.

The corrosion inhibition process is based on the adsorption of the amino acid molecules on the active sites of the metal through the nitrogen, oxygen or sulphur atoms, which form a blocking barrier to electrode’s surface.

Table 6.4. Parameter values for bronze corrosion calculated by non-linear regression of the impedance data using the equivalent electrical circuits from Figure 6.5.

Conc (mM)	**R_e (kΩ cm^2)**	**R_f (kΩcm^2)**	**C_f (μF/cm^2)**	**R_t (kΩcm^2)**	**C_d (μF/cm^2)**	**R_F (kΩcm^2)**	**C_F (mF/cm^2)**	**R_p^* (kΩcm^2)**	**IE (%)**
0	0.15	0.08	49.72	0.22	520.59	1.33	276.80	1.63	-
Cys 0.1	0.26	0.29	69.71	0.56	389.26	3.68	192.72	4.53	64.01
1	0.16	1.65	1.74	6.55	343.38	15.14	1.37	23.34	93.01
5	0.18	1.70	1.64	9.12	306.24	26.58	0.09	37.40	95.64
10	0.18	1.79	1.42	17.01	219.12	34.09	0.07	52.89	**96.92**
50	0.24	0.14	9.94	11.15	16.30	5.65	3.58	16.94	90.38
Ala 0.1	0.19	0.09	41.60	0.32	513.19	1.32	160.83	1.73	5.78
1	0.18	0.10	35.89	0.45	443.35	1.70	244.49	2.25	27.56
10	0.21	0.30	35.83	0.77	309.47	2.77	123.46	3.84	57.55
500	0.26	0.38	7.68	2.72	29.41	1.78	62.45	4.88	66.60
1000	0.33	0.41	10.55	4.81	17.95	2.96	0.27	8.18	80.07
PhAla 1	0.19	0.13	59.54	0.26	103.23	1.72	559.50	2.11	22.75
10	0.17	0.20	54.67	0.54	346.25	2.69	80.46	3.43	52.48

$^*R_p=R_f+R_t+R_F$

6.1.1.6. Amino acids as corrosion inhibitors for bronze: conclusions

From a series of six amino acids chosen for this study Cysteine (Cys), Alanine (Ala), Phenylalanine (PhAla), Methionine (Met), Arginine (Arg), Histidine (His), and Glutamic acid (Glu)), through a screening process using soil simulated environment (0.02 M NaCl and 0.125 M Na_2SO_4) at pH 8, and keeping all amino acids at 1 mM, we narrowed down our research to three amino acids as best performers: cysteine, alanine and phenylalanine. The best inhibiting amino acid from the series was cysteine.

The next step was to focus on the three amino acids found efficient in the screening: cysteine, alanine and phenylalanine at different concentrations ranging from 10^{-2} mM to 1000 mM in a the same corrosive electrolyte made of 0.2 M $Na_2 SO_4$ and 0.2 M $NaHCO_3$ used in the screening, but this time at pH 3, so we moved from the alkaline soil imitation corrosive media to a simple acid rain media.

Nevertheless, in the case of Cys, a further increase of the amino acid concentration from 10 mM to 50 mM leads to a decrease of its protective efficiency.

Each amino acid appears to have a more pronounced inhibiting effect on the cathodic process than on the anodic one, due to the fact that in strong acidic media, the amino acids are protonated at the amine group and, act mainly as cathodic inhibitors.

Comparing the impedance spectra obtained at different immersion time in the presence of the optimum concentration of Cys, it could be seen that the impedance increases with the immersion time (up to the maximum in 20 hours), and then decreases with further increase of the immersion time until it reaches, after 60 hours, a value that remains almost constant.

Further, cysteine was tested as corrosive inhibitor on bronze in the alkaline soil simulation environment (0.2 M $Na_2 SO_4$ and 0.2 M $NaHCO_3$) at pH 8. The concentrations limits for cysteine were 0.01mM, 0.1mM, and 1 mM. From EIS, OCP and PC data we conclude that cysteine does inhibit the corrosion process for concentrations of 0.1 and 0.01 mM but does not inhibit the corrosion process for bronze for a concentration of 1 mM, as it did at pH 3.

The solution pH has a strong influence on the inhibitors protection efficiency. It seems that in the case of Cysteine, the maximum inhibition efficiency at pH 3 is achieved for a concentration of 10mM and at pH 8 for a concentration of 0.01mM. The efficiency of 1mM Cys at pH 3 is higher than the maximum efficiency of 0.01mM Cys at pH 8 (93.01% *vs*. 69.53%).

6.1.2 Thiadiazoles

6.1.2.2. Thiadiazoles screening

This section is dedicated to the study of the inhibition effect on bronze of six thiadiazole derivatives (MAT, MMeT, AcAMT, PhAMT, DAT and AT.The purpose for this screening is to identify the best corrosion inhibitor among these thiadiazoles tested at a given concentration, and to compare it to BTA at the same concentration. Once the best inhibitor is identified, further tests will be performed to identify the optimum concentration and pH.

In a first step, MAT, MMeT, AcAMT, PhAMT were tested at one single concentration: 1mM, in a corrosive solution containing 0.02 M NaCl + 0.125 M Na_2SO_4 at pH 8. Diluted NaOH was used to adjust the pH. Further, two new thiadiazole derivatives (DAT and AT) were investigated.

MAT and MMeT were proven to be the best inhibitors among the investigated thaidiazoles.

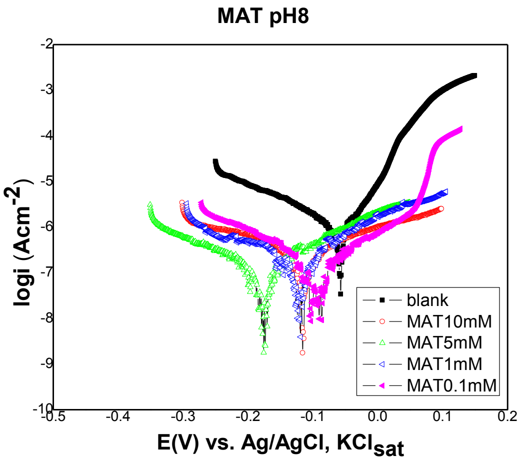


Figure 6.18: Polarization curves for bronze in 0.02 M NaCl + 0.125 M Na_2SO_4 electrolyte at pH 8, with and without MAT as inhibitor.

Table 6.13: Kinetic parameters for bronze in 0.02 M NaCl + 0.125 M Na_2SO_4 electrolyte at pH 8, with and without MAT as inhibitor.

MAT Conc. (mM)	**R_p (Ωcm^2)**	**E_{corr} (V *vs.* Ag/AgCl/KCl_{sat})**	**j_{corr} ($\mu A/cm^2$)**	**b_c (mV)**	**b_a (mV)**	**IE (%)**
0	14770	- 0.057	0.906	136.15	62.371	-
0.1	109325	- 0.092	0.126	127.45	112.14	86.48
1	44470	-0.126	0.218	206.32	164.61	66.78
5	**130519**	**-0.198**	**0.124**	**180.23**	**155.20**	**88.68**
10	56040	-0.111	0.281	232.26	183.77	73.64

Tabelul 6.14: Kinetic parameters for bronze in 0.02 M NaCl + 0.125 M Na_2SO_4 electrolyte at pH 8, with and without MMeT as inhibitor.

MMeT Conc. (mM)	**R_p (Ωcm^2)**	**R^2/N**	**j_{corr} ($\mu A/cm^2$)**	**E_{corr} (V *vs.* Ag/AgCl/KCl_{sat})**	**IE (%)**
0	14770	0.993/44	1.001	-0.050	-
0.1	2408	0.997/45	1.250	-0.06	-
1	34930	0.948/38	0.125	-0.09	57.77
5	47068	0.937/62	0.063	-0.025	68.61
10	**92250**	**0.982/48**	**0.039**	**0.001**	**83.98**

The stronger inhibitor effect of MAT compared to MMeT can be explained by the involvement of the electrons from the amino group in the conjugation with the thiadiazolic nucleus, leading to a less important participation of sulphur atoms, which become more available for the interaction with the metallic surface.

In the case of MMeT, the lack of mesomer effect (+E) reduces the ability of the organic compound to bind the metal and therefore its inhibiting effect.

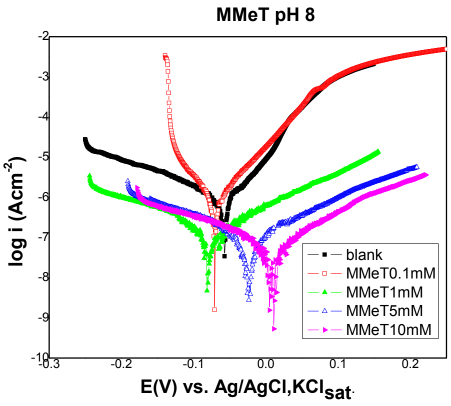


Figure 6.19: Polarization curves for bronze in 0.02 M NaCl + 0.125 M Na_2SO_4 electrolyte at pH 8, with and without MMeT as inhibitor.

6.1.2.5. Thiadiazoles as corrosion inhibitors for bronze: conclusion

Thiadiazoles, due to their chemical composition and structure, have the ability to inhibit bronze corrosion in different media composed from an array of ions, at different pH values, from aggressive acidic till neutral. It is apparent from the molecular structures that these compounds are able to get adsorbed on the metal surface through the lone pair of electrons of N and S atoms, and as a protonated species. As they contain sulphur they probably self-assemble on the bronze surface forming a protective film.

The effect of thiadiazoles is more pronounced at acidic pHs. The possible protonation equilibrium of thiadiazole derivatives which may occur in strong acidic media is presented (particularization for MMeT) in the following Scheme [44] (Figure 6.28):

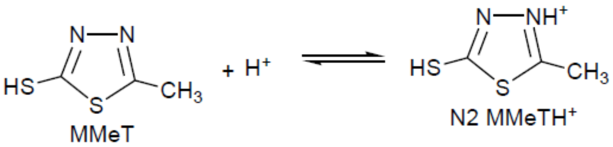


Figure 6.28.: Protonation equilibrium for MMeT [44].

From the open circuit measurements polarization curves data and EIS representations we can conclude that both MAT and MMeT inhibit the corrosion of bronze in an alkaline medium made of 0.02 M NaCl + 0.125 M Na_2SO_4. The optimum concentration for MAT is 5 mM and for MMeT is 10mM. The IE for MAT 5mM was 88.68% versus 83.98% for MMeT 10 mM.

The inhibition effect of MAT 5mM solution in 0.02 M NaCl + 0.125 M Na_2SO_4 electrolyte at pH 8 on the bronze electrode increases with the immersion time and stabilizes after less than 15 h.

DAT and AT are less effective inhibitors than the other tested thiadiazoles. The lack of electron attractive substituents in the molecule, as well as the low molecular mass of DAT and AT could be an explanation for this behavior.

6.1.3. Surfactants

Surfactants are molecules composed of polar hydrophilic group, the ‘‘head’’, attached to a nonpolar hydrophobic group, the ‘‘tail’’ [45].

The reason for selecting SDS and CTAB as an inhibitors for our study was the conflicting information about the efficiency of SDS and CTAB in acidic solutions for the inhibition of copper. Another reason is the availability of these substances on the market at very accessible prices, which is a very desirable characteristic in an inhibitor and its further applications. Also, last but not least, the fact that CTAB is not only a typical cationic surfactant but is also a quaternary ammonium salt with a long hydrocarbon chain, whose homologues have been used extensively as inhibitors against the acid corrosion of iron and steels, [46], and the fact that SDS has been studied as a corrosion inhibitor not only for copper but for pure Al and its two copper alloys [47], and all reports were favorable, qualifying these two surfactants as good corrosion inhibitors in general, made us to investigate them.

6.1.3.2. Influence of the inhibitors concentration

A. Cetyl Trimethyl Ammonium Bromide (CTAB)

Cetyl Trimethyl Ammonium Bromide (CTAB) was tested as corrosion inhibitor for bronze at different concentrations going from 10^{-3} mM to 10 mM in a simulated acid rain solution made from 31.85 mgL^{-1} H_2SO_4 +46.2 mgL^{-1} $(NH_4)_2SO_4$ +31.95 mgL^{-1}Na_2SO_4 +15.75 mgL^{-1}HNO_3 +21.25 mgL^{-1} $NaNO_3$ + 84.85 mgL^{-1}NaCl. The pH of the solutions was adjusted to 4 using diluted NaOH.

Open Circuit Potential

E_{oc} was recorded after the bronze electrode was immersed in the corrosive solution with and without various concentrations of CTAB for 1 hour. The results are presented in Table 6.22 and Figure 6.29.

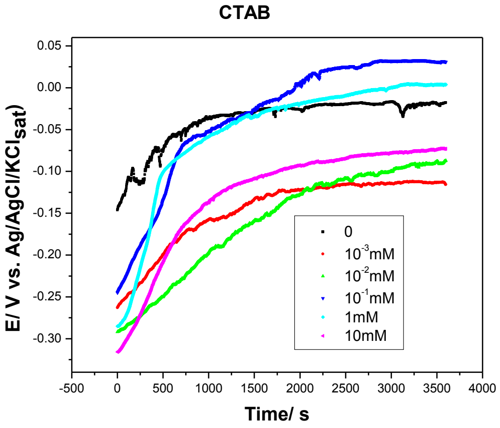


Figure 6.29: OCP curves for bronze in CTAB solutions at various concentrations.

Table 6.22: E_{oc} values for bronze in CTAB solutions at various concentrations.

No.	CTAB Conc. (mM)	E_{oc} (V *vs.* Ag/AgCl/KCl$_{sat}$)
1.	0	-0.018
2.	10^{-3}	-0.116
3.	10^{-2}	-0.087
4.	10^{-1}	0.031
5.	1	0.004
6	10	-0.073

The shift of OCP values in comparison with the blank solution could be explained by the adsorption of surfactant on the bronze surface by virtue of its hydrophobic character of the hydrocarbon chain. The results suggest that CTAB acts as a mixed-type inhibitor.

Electrochemical Impedance Spectroscopy

In order to make a complete characterization of the bronze/corrosive electrolyte interface and of the processes occurring on the electrode surface in the blank and CTAB-containing solutions, EIS measurements were carried out in a wide frequency range after the stabilization of the bronze electrode for one hour at the open-circuit potential.

The impedance spectra recorded in the blank solution and in the presence of various concentrations of CTAB are presented in Figure 6.30. The results are displayed as Nyquist diagrams.

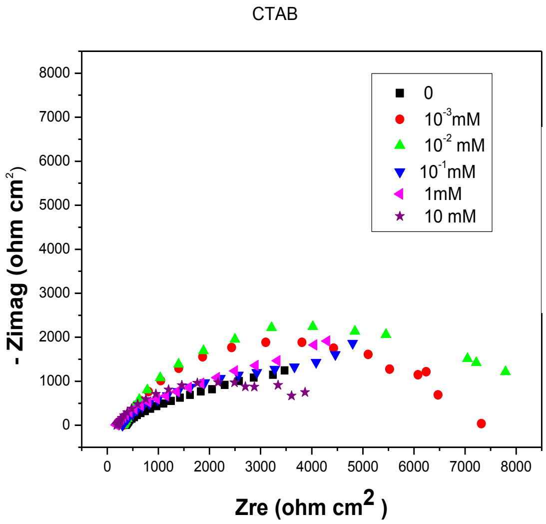


Figure 6.30: Nyquist diagrams for bronze in CTAB solutions at various concentrations.

From the EIS measurements and from the E_{oc} values we can conclude that CTAB inhibits the corrosion of bronze at all tested concentrations and at 10^{-2} mM exhibits the best inhibiting properties for bronze in an acidic corrosive solution. However, the inhibiting effect is not very strong and doesn’t vary much with the concentration of CTAB.

B. Sodium dodecyl sulfate (SDS)

Sodium dodecyl sulfate (SDS) was tested as corrosion inhibitor for bronze at different concentrations going from 1000 to 4000 ppm in the same simulated acid rain solution containing 31.85mgL^{-1} H_2SO_4 +46.2 mgL^{-1} $(NH_4)_2SO_4$ +31.95 mgL^{-1} Na_2SO_4 +15.75 mgL^{-1} HNO_3 + 21.25 mgL^{-1} $NaNO_3$ + 84.85 mgL^{-1} NaCl. The pH of the solutions was adjusted to 4 using diluted NaOH.

Table 6.23: E_{oc} values for bronze in SDS solutions at various concentrations.

No.	**SDS Conc. (ppm)**	**E_{oc} (V *vs.* Ag/AgCl/KCl$_{sat}$)**
1.	0	-0.018
2.	1000	-0.013
3	1500	0.021
4.	2000	0.008
5.	2500	0.005
6.	3000	-0.019
7.	4000	-0.003

Practically, the OCP values do not change significantly in the presence of SDS and the stabilization of the potential occurs rapidly after the immersion of the electrode in the corrosive solution. Generally, a positive potential shift appears by using SDS, suggesting a hindering of the anodic reaction (copper dissolution) due to the formation of a film of anionic surfactant on the positively charged bronze surface.

Electrochemical Impedance Spectroscopy

In order to have a complete image of the processes occurring on the electrode surface in the blank and SDS-containing solutions, EIS measurements were carried out in a wide frequency range after the stabilization of the bronze electrode for one hour at the open-circuit potential.

The impedance spectra recorded in the blank solution and in the presence of various concentrations of SDS are presented in Figure 6.32. The results are displayed as Nyquist diagrams.

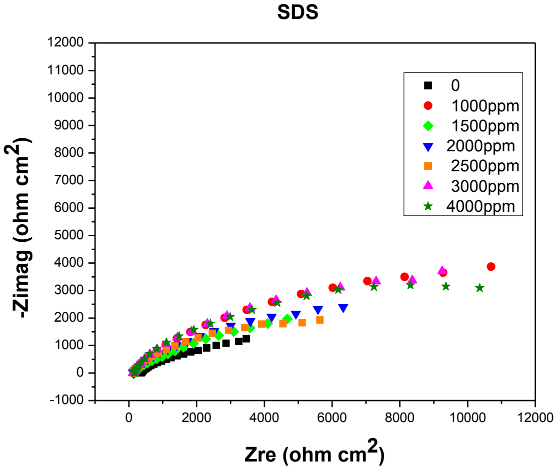


Figure 6.32.: Nyquist diagrams for bronze in SDS solutions at various concentrations.

Corroborating the results from OCP and EIS measurements we can conclude that SDS manifests relatively weak inhibiting properties in all tested concentrations and that the increase of concentration does not modify significantly the impedance spectra, possibly due to micelles formation. The critical micelle concentration (CMC) is a key indicator in determining the effectiveness of surfactants as corrosion inhibitors. Below the CMC, individual surfactant molecules or monomers tend to adsorb on exposed interfaces, so interfacial aggregation reduces surface tension and is related to corrosion inhibition. Above the CMC, the surface becomes covered with more than one monolayer and forms a protection layer on the metal surface. Consequently, the surface tension and corrosion current density are not altered significantly above the CMC. Therefore, an excellent surfactant inhibitor is one that aggregates or adsorbs at low concentrations. In other words, surfactants with low cmc values are desirable, because they adsorb at low concentrations [38].

The critical micelle concentration for SDS in pure water at 25 °C is 8.2 mM [39], but this value can be modified in electrolytes solutions. This is why an increase of the SDS concentration above a certain value does not improve the inhibiting effect of the surfactant.

Polarization Curves

In order to obtain the kinetic parameters of the corrosion process for the lowest concentration of SDS (1000 ppm), polarization curves were recorded in a potential range of ± 200 mV *vs.* OCP Figure 6.33 and the corrosion parameters were calculated Table 6.24.

The shape of the polarization curves is changed in the presence of SDS, especially in the anodic branch, suggesting that it inhibits the anodic reaction (metal dissolution). It is confirmed the fact already reported in the literature that SDS is a good anodic inhibitor at low anodic overvoltage. Moreover, the adsorption of the inhibitor follows the Langmuir isotherm [38].

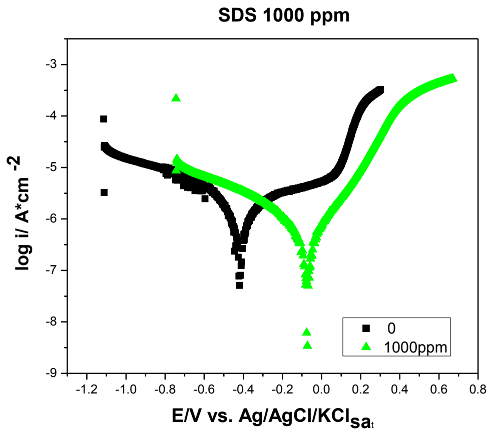


Figure 6.33: Polarization curves for bronze in the absence and in the presence of 1000 ppm SDS.

Table 6.24: Kinetic parameters for bronze in the absence and in the presence of 1000 ppm SDS.

Conc. SDS (ppm)	**R^2/N**	**E_{corr} (mV *vs.* Ag/AgCl/KClsat)**	**j_{corr} ($\mu A/cm^2$)**	**IE %**
0	0.998/19	-101.780	3.722	-
1000	0.992/65	-81.34	0.0562	98.49

Polarization curves data are in agreement with EIS data and confirm the inhibition effect of SDS at 1000 ppm. This effect is due to the rapid adsorption of the surfactant on the bronze surface (Figure 6.34).

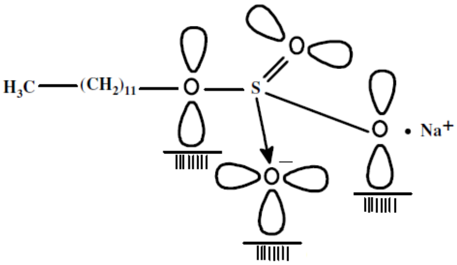


Figure 6.34: Schematic representation of the adsorption mode of SDS on a metallic surface [38].

6.1.3.3. Surfactants as corrosion inhibitors for bronze: conclusion

Both investigated surfactants (a cationic surfactant**,** Cetyl Trimethyl Ammonium Bromide (CTAB) and an anionic surfactants, Sodium Dodecyl Sulfate (SDS) exerted an inhibiting effect of bronze corrosion. The inhibition effect by surfactants is attributed to the adsorption of the surfactant molecules *via* their functional groups onto the metal surface. The adsorption rate is usually rapid and hence the reactive metal is shielded from the aggressive environment.

SDS has better inhibiting properties compared to CTAB in an acidic solution.

This result is in agreement with the research done by ***Lalitha et al***. [39], who identified SDS as being a better corrosion inhibitor compared to CTAB in acidic conditions.

The optimum concentrations found after investigations including OCP, EIS and PC were 10 $^{-2}$mM for CTAB. For SDS no important change with the concentration was noticed and its protective effect was observable from the lowest tested concentration (1000 ppm).

6.1.4. Antibiotics

In the bronze protection against corrosion, organic compounds containing nitrogen, oxygen and sulphur are proved to be the most efficient, due to their ability to form protective films on the surface of the metal [2-7].

In this study we focus on the effect of five different antibiotics (amoxicillin, ciprofloxacin, streptomycin, doxycycline and tetracycline) belonging to four different classes of clinically used drugs, as anticorrosion inhibitors on bronze. These antibiotics were previously studied as corrosion inhibitors on aluminum, cobalt-chromium alloys, stainless and mild steel, in diverse neutral or acidic media [48], but to the best of our knowledge, never on bronze.

6.1.4.2. Influence of the inhibitors concentration

a) Corrosion tests at pH 4

Polarization curves

As can be seen from Table 6.26, the corrosion potentials is shifted towards the negative direction in the presence of inhibitors. 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.

In the presence of inhibitors, in almost all cases, the values of the current density decrease, compared with bronze, this can be explained by the fact that all investigated compounds inhibit the bronze corrosion, probably forming a protective layer on the metallic surface.

The inhibiting efficiencies, calculated with equation 6.4, are not spectacular. The best IE, corresponding to the optimal concentration of antibiotics are situated around 50%.

Electrochemical impedance spectroscopy

In order to make a complete characterization of the bronze/corrosion electrolyte interface and of the processes occurring on the electrode surface in the blank and antibiotics-containing solutions, EIS measurements were carried out in a wide frequency range after the stabilization on the bronze electrode for one hour at the open-circuit potential.

The impedance spectra recorded in the blank solution and in the presence of various concentrations of antibiotics are presented in Figure 6.36 and all the results are displayed as Nyquist diagrams.

From Figure 6.36. could be seen that the impedance diagrams are characterized by a semicircular appearance with depressed capacitive loops in the entire frequency range. The larger capacitive loops sizes observed in the presence of the antibiotics might be related to an inhibition of the bronze corrosion process. Though not clearly seen in Figure 6.37, it was found that the impedance diagrams recorded in the blank solution can be suitably represented by an electric equivalent circuit corresponding to two time constants. The electrical equivalent circuit depicted in the Figure 6.37 (a) was therefore adopted to carry out a non-linear regression with a simplex method. The two parallel R-C couples are ascribed to the following contributions [23]: the high frequency contribution is attributed to the double layer capacitance (C_d) at the electrolyte/bronze interface coupled with the charge transfer resistance (R_t), whereas the low frequency elements, R_F and C_F correspond to an oxidation-reduction process taking place at the electrode surface, probable involving the corrosion products layers accumulated at the interface. R_e is the electrolyte resistance and the coefficients, n_d and n_F represent the depressed characteristic of the capacitive loops in the Nyquist diagrams.

The impedance spectra obtained in the presence of various antibiotics were fitted to an electrical equivalent-circuit including three parallel time constants (Figure 6.37 (b). Compared to the equivalent electrical circuit proposed for the blank solution, this circuit contains an additional R_f - C_f couple, which could be attributed to the dielectric character of the corrosion products (C_f, n_f) due to the formation of thin surface film (oxide and/or oxide with adsorbed inhibitor) that is reinforced by the presence of the antibiotics and by the ionic conduction through the pores of the film (R_f).

Table 6.26: Corrosion parameters measured for bronze in acid rain type electrolyte at pH 4, with and without antibiotics as inhibitors.

Sample (ppm)	**R_p (Ω cm^2)**	**R^2/N**	**E_{corr} (V vs. Ag/AgCl/KCl$_{sat}$)**	**j_{corr} (μA/cm^2)**	**b_c (mV)**	**b_a (mV)**	***IE* %**
Blank	26055	0.998/19	-0. 101	3.722	242.18	299.80	-
Doxycycline							
100	24203	0.985/39	0.069	1.530	189.09	67.43	-
200	57665	0.920/45	-0.076	0.914	132.83	86.65	**54.8**
300	35034	0.943/48	-0.085	1.277	165.55	75.81	25.6
400	29370	0.994/50	-0.131	2.420	147.40	144.22	11.2
Tetracycline							
200	34330	0.985/67	-0.153	3.596	225.38	347.41	25.2
300	36805	0.997/53	-0.111	1.360	149.05	206.23	**29.2**
400	26584	0.978/36	-0.118	1.656	140.03	132.79	1.92
500	36788	0.980/67	- 0.121	2.75	114.59	152.07	26.6
Ciprofloxacin							
200	15010	0.981/56	-0.014	2.428	135.41	76.020	-
400	36363	0.993/43	-0.021	4.469	236.86	114.85	28.3
600	39108	0.998/46	-0.073	1.732	209.16	95.07	33.3
2000	54645	0.957/48	-0.132	0.957	202.61	114.72	**52.3**
3000	21146	0.991/45	-0.200	2.550	188.49	204.40	-
Streptomycin							
50	29949	0.970/44	-0.094	2.956	193.65	212.53	12.1
100	35365	0.952/46	-0.101	3.337	233.81	251.72	26.2
200	55288	0.900/54	0.0 18	0.937	172.72	54.89	**52.8**
300	39328	0.98/47	0.00 9	1.081	197.69	64.576	33.9
400	33980	0.968/48	-0.011	1.906	382.47	83.42	23.3
Amoxicillin							
200	22274	0.995/58	0.023	1.418	152.58	51.79	-
400	29605	0.991/53	-0.006	1.003	255.696	97.620	11.4
600	28946	0.992/58	0.017	1.641	146.01	53.59	9.98
800	52110	0.986/64	0.014	1.030	178.52	45.33	**50.0**
1000	31839	0.981/67	-0.022	2.160	311.46	54.18	18.1
Cefadroxil							
200	35159	0.998/74	-0.018	2.805	157.59	124.73	25.8
400	9135	0.799/14	0.012	4.978	214.69	80.65	-
800	51114	0.935/30	-0.036	0.969	129.78	79.75	**51.32**

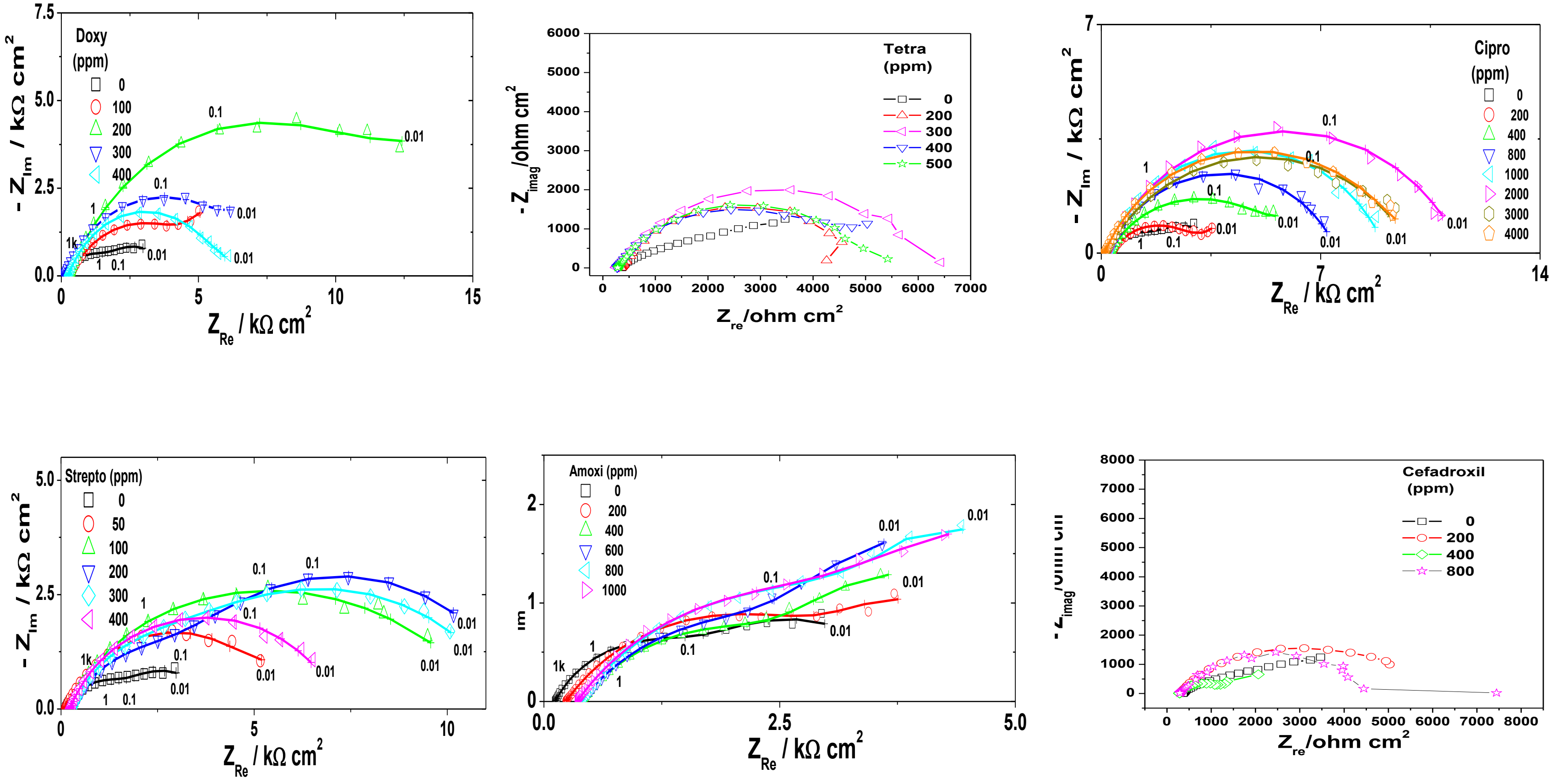


Figure 6.36: EIS evolution of bronze electrode in the corrosive solution (pH=4) in the absence and in the presence of different concentrations of antibiotics. The symbol (—+—) corresponds to the fitted data. Frequencies are expressed in Hz.

At the given angular frequency ω (rad s^{-1}) a capacitive loop is calculated, according to the equation 6.3 [15]:

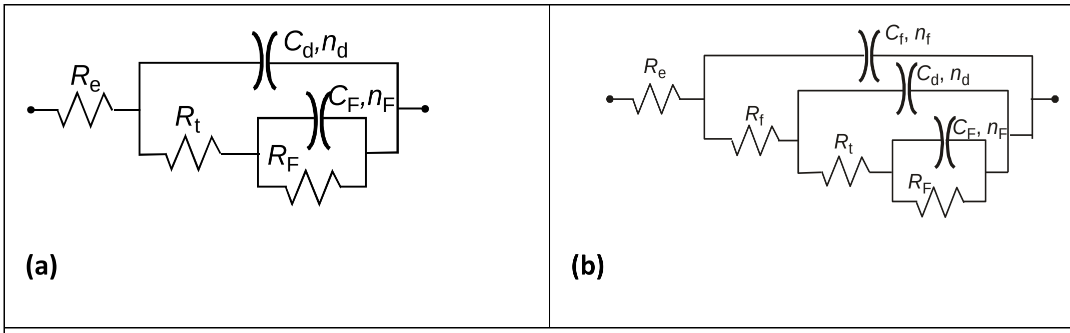


Figure 6.37: Equivalent electrical circuits used for computer fitting of the experimental data: **(a)** 2RC (for the blank) and **(b)** 3RC (in the presence of antibiotics).

The lines marked with cross in Figure 6.36 represent the calculated data with the Simplex method. The used equivalent circuits reproduce accurately the experimental impedance data corresponding to bronze corrosion in the blank and antibiotics-containing solutions, as seen in Figure 6.37, where a good overlap between the measured and calculated data was obtained.

Table 6.27 summarizes the values of the impedance parameters obtained by fitting the experimental data to the equivalent electrical circuits. The polarization resistance values, R_p calculated as the sum of $R_f + R_t + R_F$ are also presented in Table 6.27.

Data in Table 6.28 show that in most cases, disregarding the nature of the investigated organic compounds, the film resistance R_f increases with the antibiotics concentrations up to certain values, whereas the C_f value decreases. It might be possible that the surface layer covering the electrode surface in presence of the antibiotics to be thicker and more protective, which makes the ionic conduction through this layer difficult. However, at the highest concentrations of antibiotics, the R_f values tend to decrease most probably as a consequence of the deterioration of the adsorbed layer of antibiotics on the bronze surface.

The addition of the antibiotics increases the R_t values and this effect is enhanced through the increasing of the organic compounds concentration up to certain maximal values, as follows: 200 ppm *Doxy*, 200 ppm *Strepto*, 2000 ppm *Cipro*, 300 ppm *Tetra*, 800 ppm *Cefadroxil*, and 800 ppm *Amoxi*. Further increases of the antibiotics concentration leads to a decrease of the charge transfer resistance values.

In most cases, the increase of the R_t values is accompanied by a decrease of double layer capacitance C_d, which might be the due to bronze surface coverage by the antibiotics molecules, leading to a smaller area of the electrode directly in contact with the electrolyte under the corrosion product layer or to a less conductive nature of this film.

Except for the case of *Amoxi*, the faradaic resistance, R_F values generally increase with the increases of the antibiotics concentration, while simultaneously the faradaic capacitance decreases. In the case of *Amoxi*, disregarding its concentration in the corrosive solution, the values of C_F significantly increase which suggests that there is no marked protective effect towards the redox process taking place at the bronze surface, as can be also seen from the variation of R_F values which slightly changes.

The inhibition efficiency, *IE*, was calculated from the polarization resistance values, R_p, using the equation 6.4.

In the investigated experimental conditions, the highest inhibition efficiencies values obtained in the presence of the optimum concentrations of *Doxycycline* (200 ppm), *Streptomycin* (200 ppm), *Ciprofloxacin* (2000 ppm), *Cefadroxil* (800 ppm), *Amoxicillin* (800 ppm) and *Tetracycline* (300 ppm), were 54.8%, 52,8%, 52.3%, 51.3%, 50.0% and 29.2%, respectively, in agreement with the order obtained from polarization measurements as well as EIS measurements: *Doxycycline* > *Streptomycin* > *Ciprofloxacin* > *Cefadroxil* > *Amoxicillin* > *Tetracycline*.

Quantum chemical calculations

The structures of the investigated antibiotics belong to different classes of organic compounds and a direct correlation with their corrosion inhibition efficiency might not be relevant. For this reason, an independent parameter that could explain their inhibition ability should be used. Based on our previous experience [49-50], the HOMO–LUMO energy gap (ΔE_{gap}) appears to be a suitable independent parameter. Therefore, the quantum molecular parameters, such as E_{HOMO}, E_{LUMO}, ΔE_{gap} and the dipole moment were estimated by theoretical 6–31G*B3LYP DFT calculation for the optimized geometry of each investigated antibiotic.

The organic compound with the smallest gap between the HOMO-LUMO frontiers orbital can be easier involved in redox processes and therefore the parameter ΔE_{gap} could be considered for estimating the inhibition ability of different antibiotics (Figure 6.38).

Table 6.27: Parameters values for bronze corrosion of the impedance data using the equivalent electrical circuit from Figure 6.37.

Antibiotice conc. (ppm)	R_e **(kΩ cm^2)**	R_f **(kΩ cm^2)**	C_f **(µF/cm^2)**	R_t **(kΩ cm^2)**	C_d **(µF/cm^2)**	R_F **(kΩ cm^2)**	C_F **(µF/cm^2)**	R_p **(kΩ cm^2)**	***IE* (%)**
0	0.36	-	-	1.35	74.9	4.83	3420	6.18	
Amoxicilina									
200	0.23	0.11	33.2	1.02	40.4	4.36	1264	5.49	-
400	0.39	0.12	13.6	2.38	34.1	4.67	1005	7.17	13.8
600	0.40	0.37	53.2	2.05	134.7	4.53	6330	6.95	11.1
800	**0.38**	**0.44**	**33.5**	**3.31**	**45.9**	**4.92**	**6043**	**8.67**	**28.8**
1000	0.35	0.43	52.9	2.48	64.3	5.03	7564	7.94	22.2
Ciprofloxacin									
200	0.34	0.12	18.7	1.82	56.5	4.50	300	6.44	4.0
400	0.26	0.13	15.6	2.80	50.0	5.06	125	7.99	22.6
800	0.23	0.14	14.8	3.07	39.7	5.24	119	8.45	26.8
1000	0.22	0.15	13.4	5.12	28.6	5.51	110	10.78	42.7
2000	**0.26**	**0.26**	**12.1**	**7.61**	**25.2**	**6.37**	**10**	**14.24**	**56.6**
3000	0.11	0.08	20.7	5.93	27.3	6.12	18	12.13	49.1
4000	0.10	0.18	27.0	5.70	30.4	5.74	3147	11.62	46.8
Doxiciclina									
100	0.32	0.34	44.7	5.79	60.4	5.02	2710	11.15	44.6
200	**0.29**	**0.41**	**26.3**	**8.20**	**26.7**	**11.02**	**1580**	**19.63**	**68.5**
300	0.10	0.13	43.7	6.50	46.8	6.01	2161	12.64	51.1
400	0.26	0.08	41.3	5.26	25.0	2.49	2009	7.83	21.1
Streptomicin									
50	0.11	0.39	18.6	2.1	34.9	5.66	207.9	8.15	24.2
100	0.26	0.62	15.7	4.2	31.0	6.55	240.8	11.37	45.6
200	**0.30**	**0.67**	**0.9**	**5.9**	**12.5**	**8.39**	**205.0**	**14.96**	**58.7**
300	0.28	0.45	1.0	3.6	18.5	7.89	263.7	11.94	48.2
400	0.241	0.09	1.4	2.6	20.4	4.45	143.8	7.14	13.4

$^*R_p = R_f + R_t + R_F$

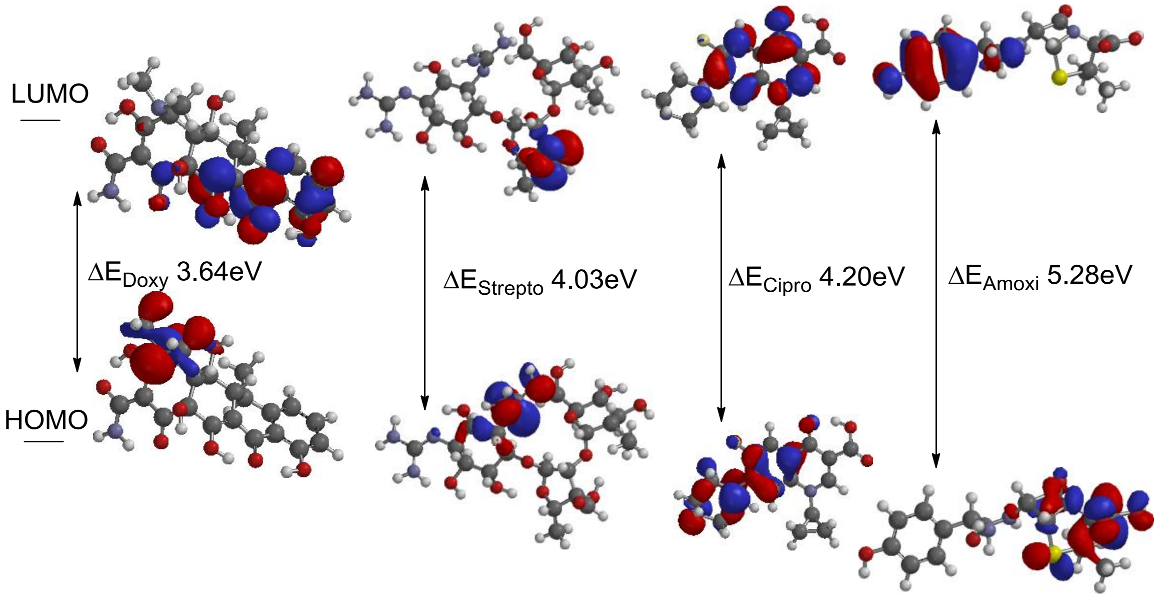


Figure 6.38: Plots of the frontier molecular orbitals for the investigated antibiotics and the values of ΔE_{gap} computed at DFT level of theory.

As shown in Table 6.28, the absolute values of the energy band gap calculated for the investigated antibiotics increase in the order: *Doxy* < *Strepto* < *Cipro* < *Amoxi*, in good agreement with the inhibition order obtained from both, electrochemical impedance spectroscopy and polarization curves techniques (Tables 6.26 and 6.27).

Table 6.28: The quantum molecular parameters for all investigated antibiotics.

Antibiotic	E (au)	E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE_{gap} (eV)
Doxy	-1564.09	-5.86	-2.22	3.64
Strepto	-2109.57	-5.34	-1.31	4.03
Cipro	-1148.40	-5.89	-1.69	4.20
Amoxi	-1559.67	-5.87	-0.59	5.28

The electrochemical measurements showed that all investigated antibacterial drugs present inhibition properties on bronze corrosion. Their inhibition efficiency is not spectacular, but their advantage is that their use could valorize expired drugs that are a risk for humans as well as for the environment.

In the investigated experimental conditions, the best inhibitor was proven to be *Doxy*, followed by *Strepto*, *Cipro*, *Cefadroxil*, *Amoxi, and Tetra*. The same inhibition order was obtained from the electrochemical techniques and quantum chemistry calculations.

b. Corrosion tests at pH 7.

This section focuses on the study of the inhibition efficiency of four antibiotics: Doxycycline, Ciprofloxacin, Tetracycline, and Streptomycin in a corrosive electrolyte imitating polluted rain, at pH 7.

Open circuit potentials

Electrochemical measurements (open circuit potential and polarization curves) were carried out using a PC controlled potentiostat PARSTAT 2273 (Princeton Applied Research, USA). The values of the open circuit potential were obtained after the bronze electrode was immersed in the corrosive solution for 1 hour. The corrosion tests were performed at room temperature.

The values of E_{oc} is presented in Table 6.29.

Table 6.29: E_{oc} values for the tested antibiotics at pH 7.

Sample	**Concentration (ppm)**	**E_{oc} (V *vs.* Ag/AgCl/KCl_{sat})**
Blank	0	- 0.154
Ciprofloxacin	200	- 0.051
	400	-0.029
	600	- 0.096
	800	- 0.076
	1000	- 0.148
	2000	- 0.077
	3000	- 0.184
Doxiciclina	100	0.010
	200	- 0.140
	300	- 0.021
	400	0.024
Tetraciclina	200	- 0.115
	300	- 0.060
	400	- 0.238
Streptomicin	50	- 0.047
	100	- 0.114
	200	- 0.020
	300	0.004
	400	- 0.034

The E_{oc} values noticed in the presence of antibiotics are more positive than those observed in the same conditions for uninhibited bronze, suggesting an inhibition of the anodic reaction and a higher corrosion resistance. The more positive shift was recorded in the case when **streptomycin** was used at **300 ppm**.

Polarization curves and electrochemical impedance spectroscopy data

Polarization measurements recorded in a potential range ± 20 mV vs. OCP allowed the evaluation of the polarization resistance, Rp.

The values of corrosion current densities (j_{corr}), corrosion potential (E_{corr}), the anodic Tafel slopes (b_a) and cathodic Tafel slopes (b_c) were calculated from the curves and are presented in Table 6.30.

From Table 6.30 one can see that the highest value for R_p was obtained in the presence of Doxycycline at 200 ppm. The inverse relationship between j_{corr} and R_p that is maintained throughout the calculations done for the above mentioned antibiotics at pH 7, suggests the consistency of polarization measurements.

The optimum concentrations of antibiotics at pH 7 were 200 ppm for *Doxy*, 600 ppm for *Cipro*, 200 ppm for *Strepto* and *Tetra.*

From the inhibition efficiency values calculated with the equation 6.2, the order of the inhibitory effect is *Doxy* > *Strepto* > *Cipro* > *Tetra.*

Cipro 400 ppm and *Tetra* 200 ppm, at pH 7 do not seem to inhibit the corrosion of bronze.

Electrochemical impedance spectroscopy measurements were carried out in a wide frequency range after the stabilization of the bronze electrode for one hour at the open-circuit potential.

In Figure 6.40 are presented the NYQUIST plots recorded for the bronze electrode in the absence and in the presence of ciprofloxacin, doxycycline, streptomycin and tetracycline at pH 7.

The impedance diagrams are characterized by a semicircular appearance with depressed capacitive loops in the entire frequency range. A qualitative evaluation of the impedance spectra allowed estimating the optimum concentrations of antibiotics, which are: 200 ppm for *Doxy*, 600 ppm for *Cipro*, 200 ppm for *Strepto* and *Tetra.*

These results were in agreement with those obtained from the polarization measurements.

Doxycycline has the best inhibiting properties with an inhibition efficiency of 60.6%

Table 6.30: Corrosion parameters measured for bronze in 0.0462 g/L $(NH_4)_2SO_4$ + 0.03195 g/L Na_2SO_4 + 0.02125 g/L $NaNO_3$ + 0.08485 g/L NaCl + 0.03185 g/L H_2SO_4 + 0.01575 g/L HNO_3, with and without antibiotics, at pH 7.

Conc. (ppm)	R_p (Ω cm^2)	R^2/N	E_{corr} (Vvs.Ag/AgCl/KClsat)	j_{corr} (μA/cm^2)	b_c (mV)	b_a (mV)	IE %
Blank	44992	0.975/75	0.018	0.977	110.60	94.366	
Ciprofloxacin							
200	45094	0.998/75	-0.0 29	0.969	326.99	191.75	0.81
400	16891	0.974/36	- 0.034	3.54	300.21	140.04	-
600	60099	0.970/57	- 0.095	0.639	182.02	298.37	**34.5**
800	52376	0.984/54	- 0.088	0.876	170.48	101.69	10.3
1000	45835	0.990/52	-0.207	0.967	152.64	152.86	0.80
2000	45060	0.998/74	-0.114	0.972	117.57	89.768	0.51
3000	53850	0.999/34	-0.184	0.758	179.36	147.44	22.4
Doxycycline							
100	65947	0.991/66	0.021	0.629	113.48	88.737	35.6
200	**96571**	0.973/71	0.0 13	0.385	126.20	160.07	**60.6**
300	46254	0.990/73	- 0.046	0.687	207.89	245.10	29.7
400	77101	0.998/71	0.029	0.522	120.20	122.77	46.5
Tetracycline							
200	55643	0.922/18	-0.095	0.883	101.22	214.63	9.62
300	46863	0.987/56	-0.027	0.923	236.19	81.161	5.52
400	24473	0.991/72	-0.199	3.389	221.83	228.94	-
Streptomycin							
50	56478	0.973/46	- 0.009	0.776	153.48	84.464	20.5
100	45103	0/962/40	- 0.065	0.967	99.291	144.83	1.02
200	67796	0.996/70	- 0.009	0.654	152.21	100.10	**33.6**
300	59451	0.999/73	0.002	0.723	171.88	89.855	25.9
400	48971	0.977/47	- 0.096	0.889	141.48	152.103	9.01

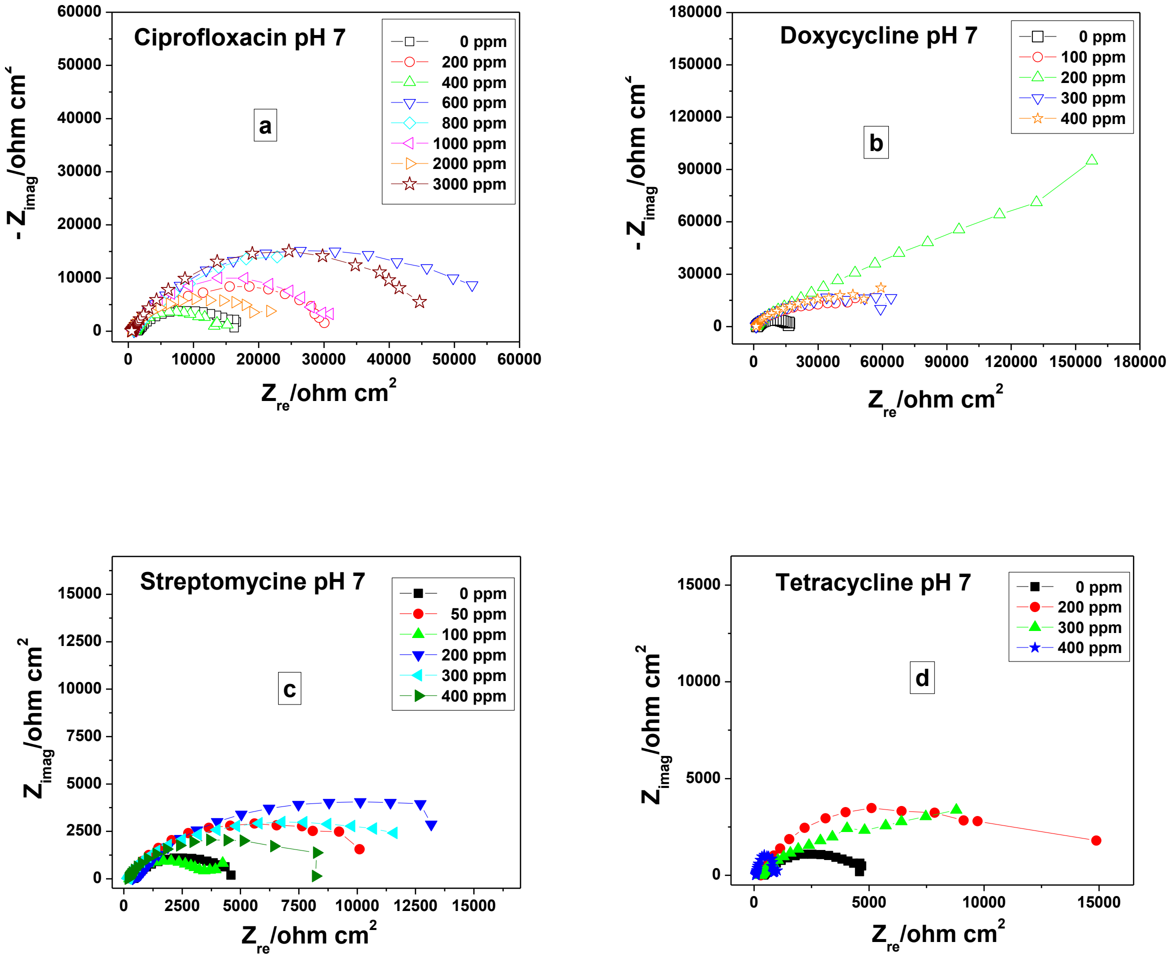


Figure 6.40: EIS evolution of bronze electrode im the corrosive solution (pH=7) in the absence and in the presence of differents concentrations of antibiotics.

a) Corrosion tests at pH 9

The antibiotics studied at pH 9 as corrosion inhibitors for bronze in an polluted rain imitation electrolyte made from 0.0462 g/L $(NH_4)_2SO_4$ + 0.03195 g/L Na_2SO_4 + 0.02125 g/L $NaNO_3$ + 0.08485 g/L NaCl + 0.03185 g/L H_2SO_4 + 0.01575 g/L HNO_3 (pH 9) were ciprofloxacin, doxycycline and streptomycin at different concentrations.

Open circuit potential

OC potentials were recorded and the results are presented in Table 6.31.

Table 6.31: E_{oc} values for the tested antibiotics at pH 9.

Compound	**Concentration (ppm)**	**E_{oc} (V *vs.* Ag/AgCl/KCl_{sat})**
Blank	0	- 0.153
Ciprofloxacin	200	- 0.078
	400	- 0.135
	600	- 0.107
	800	- 0.090
	1000	- 0.106
	2000	- 0.165
	3000	- 0.272
Doxycycline	100	- 0.074
	200	- 0.090
	300	- 0.035
	400	0.047
Streptomycin	50	- 0.021
	100	- 0.044
	200	- 0.069
	300	0.020
	400	- 0.038

As seen from the above table, in almost all cases a positive shift of the open circuit potential compared to pure bronze is noticeable, suggesting a film formation on bronze surface that hinders the anodic reaction (dissolution of bronze). Only in the case of C*ipro*, we noticed that the values of E_{oc} for *Cipro* at 2000 ppm, 3000 ppm are slightly more negative than that of bronze.

Polarization curves

Polarization curves were recorded for *Cipro*, *Doxy* and *Strepto* at different concentrations at pH 9. The results are presented in Table 6.32.

Table 6.32: Corrosion parameters measured for bronze in 0.0462 g/L $(NH_4)_2SO_4$ + 0.03195 g/L Na_2SO_4 + 0.02125 g/L $NaNO_3$ + 0.08485 g/L NaCl + 0.03185 g/L H_2SO_4 + 0.01575 g/L HNO_3, with and without antibiotics, at pH 9.

Conc. (ppm)	**R_p (Ω cm^2)**	**R^2/N**	**E_{corr} (V *vs.*Ag/AgCl/KCl$_{sta}$)**	**j_{corr} (μA/cm^2)**	***b*$_c$ (mV)**	***b*$_a$ (mV)**	**IE %**
Blank	49110	0.975/75	0.008	1.793	194.18	229.71	
Ciprofloxacin							
200	74876	0.996/67	-0.088	1.194	112.26	315.09	**33.4**
400	63335	0.951/74	-0.098	1.332	178.21	436.14	25.7
600	69041	0.987/74	-0.064	1.724	212.61	410.63	3.8
800	28540	0.984/74	-0.108	2.581	233.71	115.49	-
1000	55942	0.983/74	-0.095	1.733	129.89	216.11	3.6
2000	64178	0.991/68	-0.147	1.246	197.83	131.63	16.5
3000	50406	0.993/73	-0.245	1.698	176.06	360.64	5.3
Doxycycline							
100	56081	0.968/69	-0.053	0.896	104.12	166.74	50.02
200	53717	0.943/59	-0.039	0.967	124.82	190.78	46.1
300	56517	0.974/63	-0.047	0.817	118.08	258.04	54.4
400	95996	0.962/50	0.094	0.319	158.79	101.71	**82.1**
Streptomycin							
50	101153	0.997/74	-0.019	1.028	187.48	257.55	51.4
100	75105	0.995/73	-0.038	1.146	185.09	247.02	36.0
200	279853	0.985/76	-0.051	0.315	114.82	81.160	**82.4**
300	71144	0.998/71	0.011	0.878	161.59	85.170	30.9
400	49386	0.997/70	-0.035	1.679	232.01	45.490	6.35

Electrochemical impedance spectroscopy (EIS)

Electrochemical impedance spectra were recorded after one hour stabilization of bronze at the open circuit potential**.** Figure 6.42 presents the Nyquist plots for *Cipro*, *Doxy* and *Strepto* solutions, at various concentrations, in the polluted acid rain electrolyte, at pH 9.

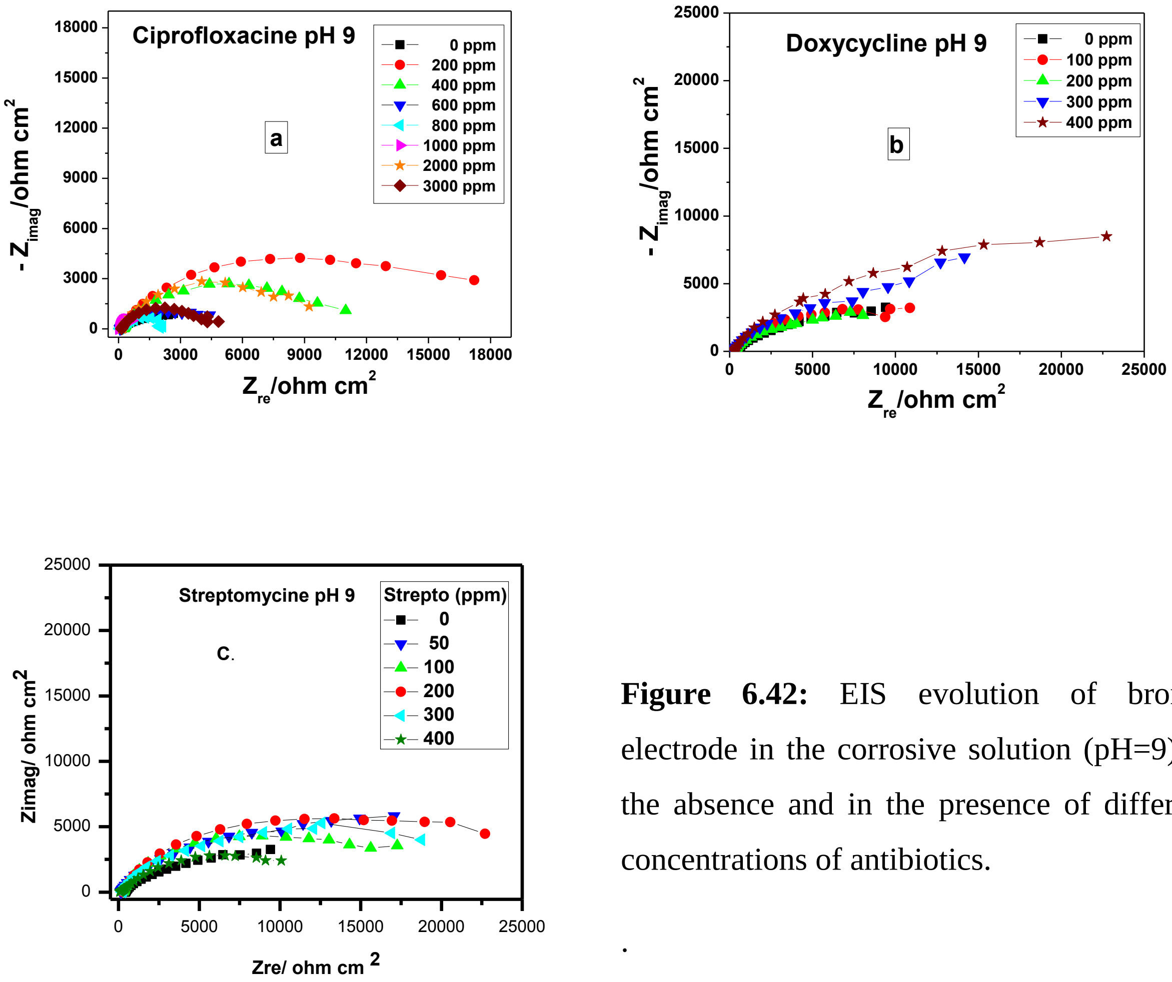


Figure 6.42: EIS evolution of bronze electrode in the corrosive solution (pH=9) in the absence and in the presence of different concentrations of antibiotics.

The optimal concentrations for the antibiotics at pH 9 were found to be the following: 200 ppm for *Strepto*, 400 ppm for *Doxy* and 200 ppm for *Cipro*. However, *Strepto*, *Doxy* and *Cipro* exhibit only a moderate anticorrosive effect on bronze.

The inhibition order of the investigated antibiotics is: *Strepto* (200 ppm) > *Doxy* (400 ppm) > *Cipro* (200 ppm) and the inhibiting efficiencies, calculated with the equation (6.2), are 82.4; 82.1 and 33.4 respectively. The highest value of R_p was noticed for streptomycin at 200 ppm. This situation illustrates the importance of electrolyte pH on the protective effect of the antibiotics in bronze corrosion.

6.1.4.5. Antibiotics as corrosion inhibitors for bronze: conclusions

The tested antibacterial drugs are proved to be one eco friendly solution for protecting metals from corrosion. Their affinity to adsorb onto bronze surface make them very attractive to be used as corrosion inhibitors on bronze surfaces. Even if their efficiency is not spectacular, (the best values are around 50% at pH 4 and 80 % at pH 9), they could be used after expiration date, when their use for therapy is not allowed any more.

The inhibiting effect of antibiotics is time-dependent. The best inhibitor was *Doxy* (for pH 4 and 7), at its optimal concentration (200 ppm), after 1 h of immersion in the corrosive solution.

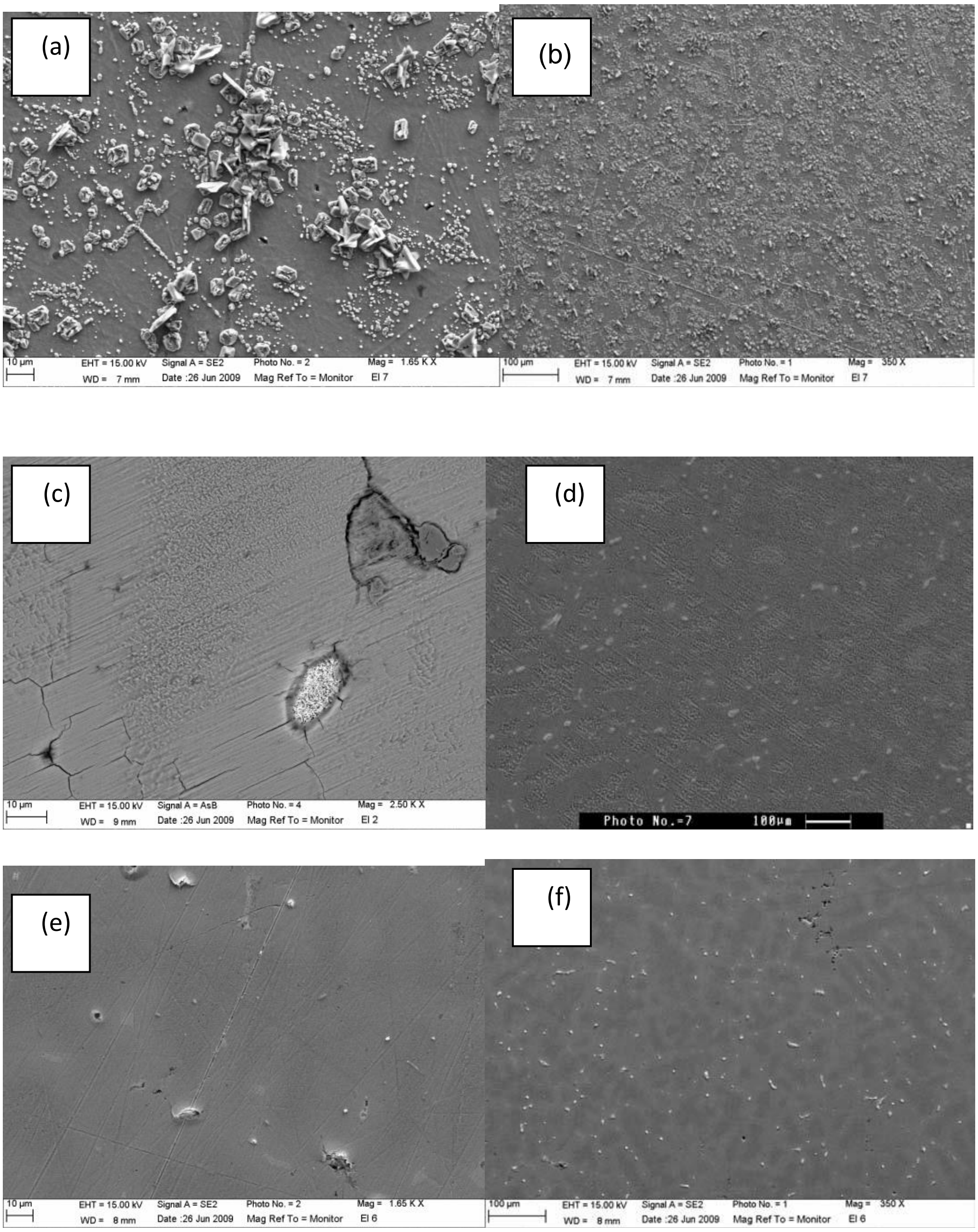
6.2. Morphological characterization of corrosion products

In order to investigate the metallic surface and to determine whether a change in its aspect has happened after the immersion of the electrode in the electrolyte, SEM analysis of the bronze surface in the presence and in the absence of amino acids and antibiotics, after 66 and, respectively, 72 hours immersion in two different corrosive solutions were carried out.

6.2.1. SEM analysis of bronze surface in the presence and absence of amino acids

The corrosive solutions used on bronze were made of 0.2 g/ L Na_2SO_4 + 0.2 g/L $NaHCO_3$, and acidified to pH 3, to which different concentrations of amino acids were added. The concentrations used for the different amino acids were determined previously as optimal and they are : Cys 0.1 mM and10 mM, and 1mM PhAla.

Figure 6.46 a and b presents the bronze surface morphology after 66 hours of immersion in the corrosive solution in the absence of any organic compounds. It can be seen that in the absence of any inhibitor the bronze surface is covered with a layer of corrosion products. The slight inhibiting effect exerted by low concentrations of PhAla (1mM) (Figure 6.46 c and d) and Cys (0.1 mM) (Figure 6.46 g) reduced the roughness of the bronze surface. In contrast, in the presence of the optimum concentration of Cys (10 mM) almost no corrosion is visible on the metallic surface (Figure 6.46 e and f), confirming the inhibiting efficiency of Cys at this concentration, which is in agreement with the electrochemical results presented in section 6.1.1.3.



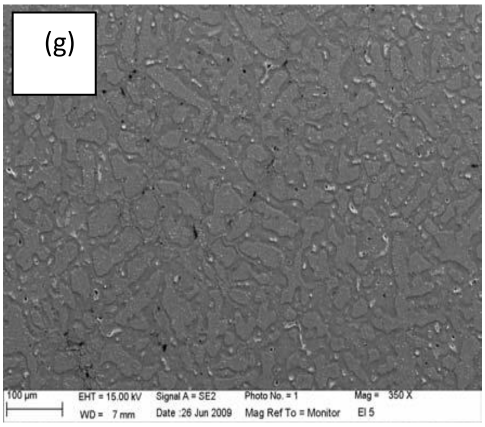


Figure 6.46: SEM micrograph of the bronze surface obtained after 66 hours immersion in 0.2 g/L $NaHCO_3$ + 0.2 g/L Na_2SO_4 (pH 3) in the absence (a and b) and in the presence of: (c and d) 1 mM PhAla , (e and f) 10 mM Cys, and (g) 0.1 mM Cys.

6.2.2. SEM analysis of bronze surface in the presence and absence of antibiotics

In the case of antibiotics the corrosive solution used was 31.85 mgL^{-1} H_2SO_4 + 46.2 mgL^{-1} $(NH_4)_2SO_4$ +31.95 $mgL^{-1}Na_2SO_4$ + 15.75 $mgL^{-1}HNO_3$ +21.25 $mgL^{-1}NaNO_3$ + 84.85 mgL^{-1}NaCl at pH 4, and as inhibitors we used *Doxy* and *Strepto,* at their optimum concentrations of 200 ppm.

Figure 6.47 presents the surface morphology of bronze after 72 hours immersion in the corrosive solution (pH=4), in the absence and in the presence of the optimal concentrations of *Doxy* and *Strepto*.

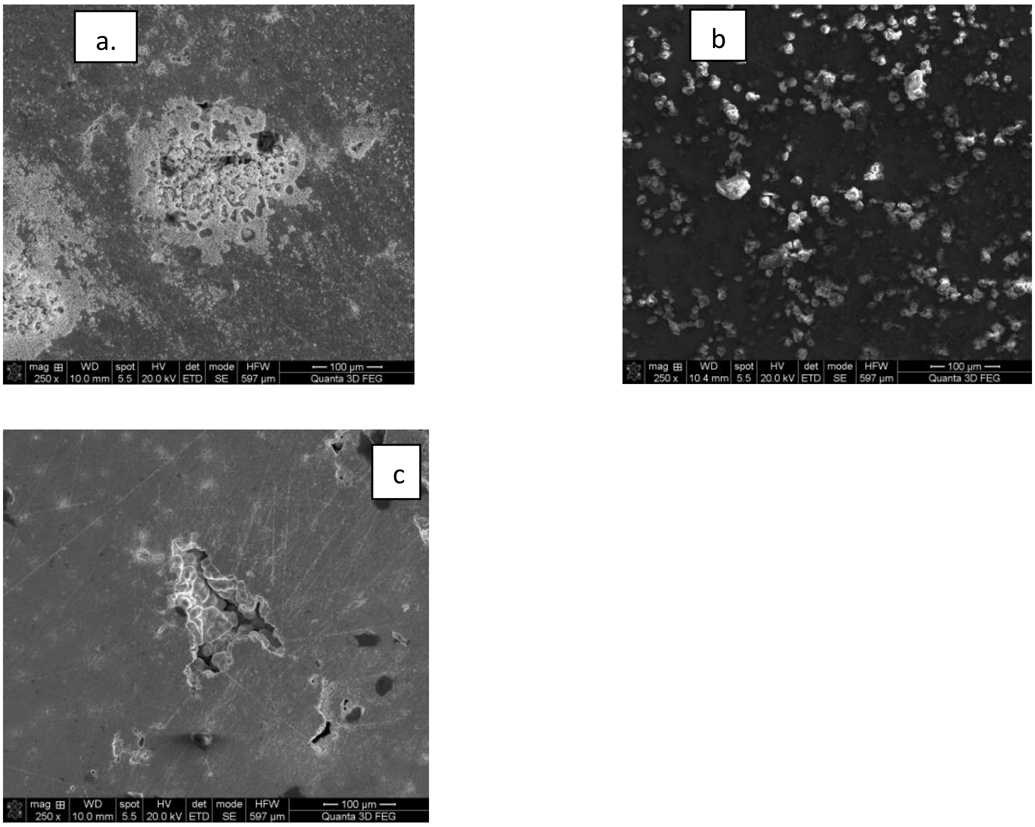


Figure 6.47: SEM images of bronze surface obtained after 72 hours immersion in corrosive solution (pH 4) in the absence (a) and in the presence of 200 ppm *Doxy* (b) and 200 ppm *Strepto* (c).

From SEM pictures taken after 72 hours immersion of the bronze surface in corrosive solution it could be seen that in all cases, after this period, the bronze surface is already covered with a layer of corrosion products. The use of *Doxy* and *Strepto* at a concentration level of 200 ppm leads to a diminished production of corrosion products on the surface comparing to the blank material. However, the improvement is not spectacular.

7. Conclusions

This study focused on finding innoxious organic inhibitors for bronze corrosion belonging to four major categories of compounds: amino acids, thiadiazoles, surfactants and antibiotics. These categories were chosen based on their structure, since it was proven that organic compounds containing O, S and N have a better inhibition on bronze corrosion. Several of these compounds were studied before as corrosions inhibitors, but never for bronze, others were used for the first time as corrosion inhibitors.

The range of concentrations, the three pH values: acidic, neutral and alkaline used for each inhibitor, and the variety of electrolytes imitating polluted environments, makes this study a complex one, offering a good image of what these inhibitors have to offer in the domain of bronze corrosion.

Amino acids

1. Among the six tested amino acids, the best protective efficiency was observed in the case of Cys, followed by Ala and PhAla. The corrosion inhibition efficiency of the amino acids depends on their chemical structure and decreases in the following order: Cys > Ala > PhAla.
2. The optimum concentrations for the amino acids depend on the composition of the corrosive environment and on the pH. In the case of Cysteine, the maximum inhibition efficiency at pH 3 is achieved for a concentration of 10 mM and at pH 4 for a concentration of 1mM, using acid rain with two different compositions. At pH 8 the optimum concentration was 0.01mM. The highest inhibition efficiency was achieved at pH 3 by 10 mM cysteine (96.92%)
3. The good anticorrosive protection of Cys on bronze corrosion is probably a consequence of its adsorption on the electrode as bidentate ligand in which surface coordination is taking place through both the amino group and the –S– moiety
4. Each amino acid appears to have a more pronounced inhibiting effect on the cathodic process than on the anodic one. This could be explained considering the fact that amino acids are protonated at the amine group and could be adsorbed on the cathodic sites of bronze, acting mainly as cathodic inhibitors. The adsorption of the amino acid molecule on the active sites of the metal could be possible not only through the nitrogen atom, but also through the oxygen or through the mercapto group present in its structure, forming a protective film on the metal surface.

The efficiency of cysteine increases with the immersion time, up until 20 hours, and then decreases with further increase of the immersion time until it reaches, after 60 hours, a value that remains almost constant.

Thiadiazoles

Six different thiadiazoles: MAT, MMeT, AcAMT, PhAMT , DAT and AT were investigated in a variety of concentrations, corrosion solutions and pHs. AT and DAT were tested as corrosion inhibitors on bronze for the first time.

1. All thiadiazoles present good corrosion inhibition properties for bronze.
2. In an alkaline electrolyte, the optimum concentration for MAT is 5 mM and for MMeT is 10mM. The IE for MAT 5mM was 88.68% versus 83.98% for MMeT 10 mM.
3. The inhibition effect of MAT 5mM at pH 8 on the bronze electrode increases with the immersion time.
4. The inhibition effect of DAT is higher compared to AT due to the existence in its structure of an extra group amino that can be adsorbed on the metal's surface.
5. In acid rain at pH 4 AT's optimum concentration for the inhibition of bronze corrosion was 1mM and the inhibiting efficiency decreased with the increasing value of the concentration. For DAT, the optimum concentration was 10 mM, At concentrations higher than 10mM, as of 15 or 20 mM, DAT does not inhibit the corrosion process, but actually it stimulates it. At concentrations lower than 10 mM DAT shows inhibitory properties but less than the results obtained at 10 mM.
6. At pH 7, the best efficiency as corrosion inhibitor was the 10 mM DAT and the 0.1 mM AT. All other concentrations for DAT and AT at pH 7 showed no inhibiting properties, actually they favored the corrosion of bronze.
7. Because of their molecular structures, these compounds are able to get adsorbed on the metal surface through the lone pair of electrons of N and S atoms.

Surfactants

Very little literature about SDS and CTAB used as corrosion inhibitors for copper was found, and the information was conflictual. No research surfaced about surfactants used as corrosion inhibitors for bronze. After our investigations using SDS and CTAB as inhibitors for bronze corrosion we conclude that:

1. The inhibiting effect of CTAB is relatively modest in acid electrolyte at pH 4.
2. SDS showed very high inhibiting properties in an acidic solution, the value of j_{corr} decreasing by a factor of 100 compared to the blank.
3. The optimum concentrations were 10 $^{-2}$mM for CTAB and 1000 ppm for SDS.
4. SDS undergoes adsorption on the positively charged copper surface through the negatively charged part of its hydrocarbon chain, forming a barrier on the copper surface. In the case of CTAB, the bromide ions will adsorb at copper/solution interface and through this adsorption they increase the inhibiting tendency of the ammonium ions through a synergistic effect.

Antibiotics

This research presents in premiere a study of antibiotic drugs as corrosion inhibitors for bronze.

1. All tested antibiotics, belonging to different categories of drugs, showed inhibiting properties for bronze corrosion at pH 4, 7 and 9.
2. The concentrations of the most efficient drugs were very small, in the range of 200 ppm, making this aspect, together with the non toxicity, availability and low cost of antibiotics another plus in considering these substances as corrosion inhibitors.
3. At pH 4 and 7 Doxycycline was the most efficient inhibitor (200ppm), followed by Streptomycin (200 ppm) and Ciprofloxacin (2000 ppm and 600ppm, respectively). At pH 9 Streptomycin had the highest inhibition efficiency (200 ppm), followed by Doxycycline (400 ppm), and Ciprofloxacin (200 ppm).
4. The highest inhibition efficiency was obtained for Streptomycin at pH 9 (82.4%)
5. The antibiotics with the highest molecular mass: Doxycycline (M= 952.86 g/mol) and Streptomycin (M= 1457.14 g/mol) proved to have the best inhibitory properties for bronze in corrosion environments with pH values from acidic to alkaline. The adsorption of these molecules on the metal's surface was done through the nitrogen and oxygen atoms in their structures.
6. In time the corrosion behavior of antibiotics varies with the type of drug and with the pH. At pH 4 the inhibition efficiency of all tested antibiotics decreases with time, except for Tetracycline, where a steep increase of IE was noticed after 72 hours. At pH 7 there was no modification of the inhibition properties in time for Doxycycline and

Streptomycin, and an increase of the efficiency with time for Tetracycline and Ciprofloxacin.

7. Capacitatea de inhibare in timp variaza cu tipul de antibiotic si cu pH-ul. La pH 4 eficienta de inhibare a coroziunii demonstrate de antibiotice scade cu cresterea timpului de imersie, cu exceptia Tetraciclinei pentru care s-a observant o crestere marita a capacitatii de inhibare la limita de 72 de ore. La pH 7 nu s-a observant nici o modificare a capacitatii de inhibare cu trecerea timpului pentru Doxiciclina si Streptomicina, iar pentru Tetraciclina si Ciprofloxacina s-a observant o crestere a capacitatii de inhibare in timp.

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