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Environmentally-Safe Corrosion Inhibitors for the Protection of Bronzes against Corrosion in Acidic Media

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Abstract: The inhibiting proprieties of two innoxious amino acids (cysteine and phenylalanine) as bronze corrosion inhibitor in a strong acidic solution of 0.2 g/L Na_2SO_4 + 0.2 g/L $NaHCO_3$ at pH=3 was studied by open-circuit potential measurements, electrochemical impedance spectroscopy and SEM analysis. The impedance measurements revealed that the bronze interface in the absence and in the presence of the amino acids could be suitably represented by a (3RC) equivalent electrical circuit. The magnitude of polarization resistance values determined from the impedance spectra and, consequently, the inhibition efficiencies were found to depend on the structure of amino acids. The anticorrosive efficiencies of the investigated compounds decrease in the order: Cys (96.91 %) > PhAla (52.22 %). SEM analysis of the bronze surface revealed that amino acids inhibit the bronze corrosion process, due to their ability to adsorb on the metallic surface. The results are consistent with the significant increase of impedance in the presence of the organic inhibitors.

Keywords: bronze, corrosion, amino acids, electrochemical impedance spectroscopy, SEM

1. Introduction

Copper and copper-based alloys are commonly used to produce heat exchangers, building construction, electronics, coinage, art works etc. [1].

In spite of the fact that copper is a relatively noble metal, its corrosion resistance diminishes when the aggressive solution concentration increases.

Typical corrosion inhibitors for copper and its alloys are heterocyclic compounds containing nitrogen, oxygen or sulphur atoms [2-3]. The effectiveness of these organic molecules is based on their ability to form a protective film by several mechanisms (*i.e.* adsorption, polymerization etc.).

Nevertheless, an important disadvantage of heterocyclic compounds is their toxicity and the lack of biodegradability [4-6].

Increasing awareness of the health and ecological risks has drawn attention to finding more suitable inhibitors, which are nontoxic [7]. In this context, several works focused on the investigation of the amino acids as corrosion inhibitors of iron [8], steel [9-12], aluminum [7], lead [13], copper [6, 14-19] and its alloys [20] in various aggressive media. Amino acids are innoxious, biodegradable, soluble in aqueous media, relatively cheap and easy to produce at high purity [21].

The investigations revealed that cysteine is the most efficient corrosion inhibitors of copper in neutral and acidic chloride solutions, due to its physical adsorption on the metallic surface via the mercapto- group in its molecular structure. For instance, cysteine has found to act as cathodic-type inhibitor for copper corrosion and its maximum inhibition efficiency (84%) was achieved at concentrations of about 16 mM in 0.6 M NaCl and at 18 mM in 1 M HCl, respectively [14]. The adsorption of cysteine on the copper surface in neutral and acidic chloride solutions obeys the Langmuir adsorption isotherm. Matos et al. [15] reported that at low polarisation cysteine inhibits the anodic dissolution of copper in sulfuric acid media due to formation of the cysteine–Cu (I) intermediate. At high overpotentials, cysteine has no influence on anodic process.

Furthermore, in recent papers [22-23] we have reported the beneficial effect exerted by several amino acids, *i.e.* cysteine (Cys), glutamic acid (Glu), methionine (Met), histidine (His), arginine (Arg) and alanine (Ala) on bronze corrosion in weak acidic electrolyte. We have found that the protection effectiveness of the amino acids on bronze corrosion strongly depends on their molecular structure, particularly on the size and electronic effects of the substituents in molecule, as shown in the following sequence: Cys > Glu > Met > Arg > His [22].

The efficiency of the amino acids as corrosion inhibitors depend among other parameters, on solution pH, because it may determine a corrosion mechanism, the state of metallic surface, as well as the state of inhibitor molecule (protonated, deprotonated) [24].

In this context, continuing our previous works on the use of amino acids as environmentally-safe corrosion inhibitors of bronze, we have studied the anticorrosive properties of cysteine (Cys) and phenylalanine (PhAla) in a strong acidic solution of 0.2 g L^{-1} Na_2SO_4 + 0.2 g L^{-1} $NaHCO_3$ at pH = 3.

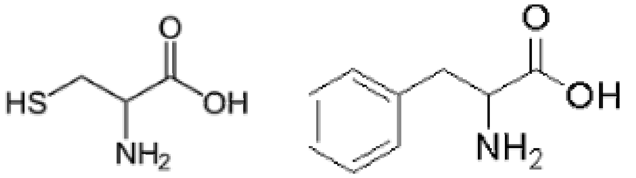
The electrochemical behavior of bronze in the absence and in the presence of different concentrations of amino acids was studied by open-circuit potential and electrochemical impedance spectroscopy measurements. A scanning electron microscope (SEM) was used for the surface analysis.

2. Experimental

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=3 by addition of dilute H_2SO_4. The solution was prepared using analytical grade reagents (Merck, Darmstadt, Germany) and ion-exchanged water.

Amino acids (Sigma Aldrich, UK) were dissolved in the electrolyte solution to the concentrations range of 0.1 - 50 mM, depending on the compounds solubility limit.

The molecular structures of the amino acids are shown in scheme 1.



Cysteine (Cys) Phenylalanine (PhAla)

Scheme 1. Molecular structure of the investigated amino acids

An electrochemical cell with a three-electrode configuration was used; the working electrode was made of bronze (S = 0.283 cm^2) with the chemical composition presented in Table 1; a large platinum grid and a saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively.

TABLE 1. Chemical composition (% at) of bronze working electrode

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

Electrochemical experiments were performed at room temperature, using a PAR model 2273 potentiostat (USA) controlled by a PC computer.

Electrochemical impedance spectroscopy measurements (EIS) were carried out at the open circuit potential after 1 hour immersion of the bronze electrode in the corrosive medium. The impedance spectra were acquired in the frequency range 100 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 software based on a Simplex parameter regression.

For morphological studies, the bronze surface was prepared by keeping the electrodes for 66 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 apparatus.

3. Results and Discussion

3.1. Open-circuit potential measurements

The evolution of the open circuit potentials (ocp) for bronze over 1 hour immersion in the corrosive solution without and with the addition of amino acids at different concentrations is illustrated in Fig. 1.

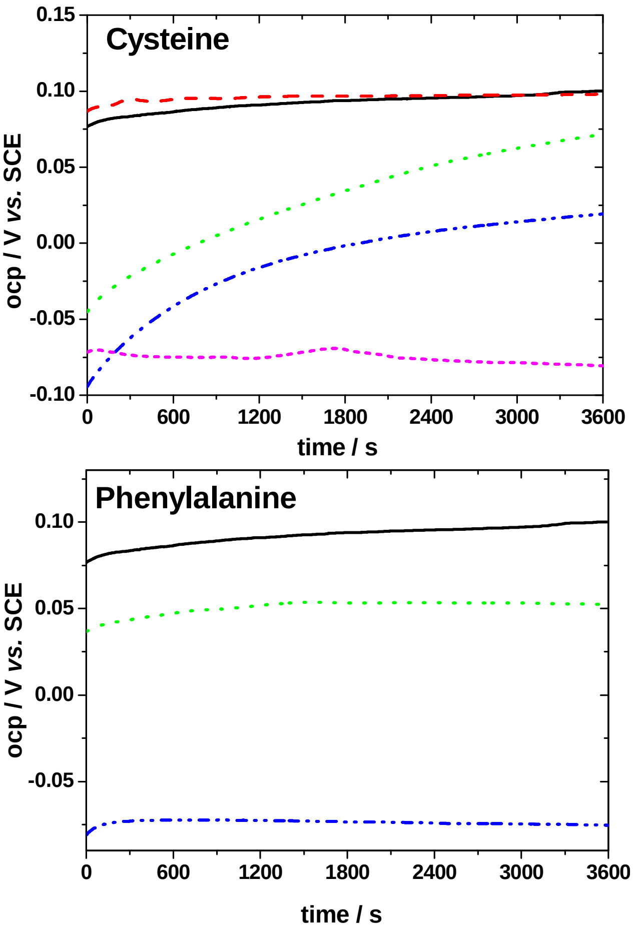


Figure 1. Variation of the open-circuit potential in time for bronze electrode after immersion in the corrosive media in the absence and in the presence of amino acids at different concentrations of amino acids (mM):(□□) 0; (— —) 0.1; (·····); 1; (—·•—) 10; (-----) 50.

As it can be seen in Fig. 1, the open-circuit potential shows the same trend in all the solutions, it gets more negative with time, until it reaches a steady state value.

The value of the steady-state potential (E_{ss}) of bronze in blank solution was + 0.100 mV vs. SCE. The addition of the amino acid in the corrosive media shifts the steady state potentials towards more negative values as compared to E_{ss} values obtained in inhibitor-free electrolyte. This behaviour is likely to be ascribed to a slow down of the reaction rate of the cathodic process due to the inhibiting effect of amino acid molecules and/or the deposition of corrosion products on the electrode surface [20].

E. Oguzie et al. [9] showed that a precise categorization of a compound as an anodic or cathodic inhibitor requires an E_{ss} displacement of up to 85mV with respect to the blank corrosive solution.

The magnitude of the E_{ss} displacements suggests that at low concentrations (0. 1-1 mM), the amino acids simultaneously affect the cathodic and anodic reactions, while at higher concentrations they predominantly influence the cathodic reduction, probably acting as barriers to the diffusion of oxygen molecules from the solution to the bronze surface.

3.2. Electrochemical impedance spectroscopy measurements

In order to obtain information on the electrochemical processes taking place at the bronze interface in the absence and in the presence of amino acids, electrochemical impedance spectroscopy (EIS) were carried out. The measurements were conducted at the open-circuit potentials and the obtained Nyquist plots are depicted in Fig. 2. The insets present the high frequency domain of impedance spectra in enlarged scale.

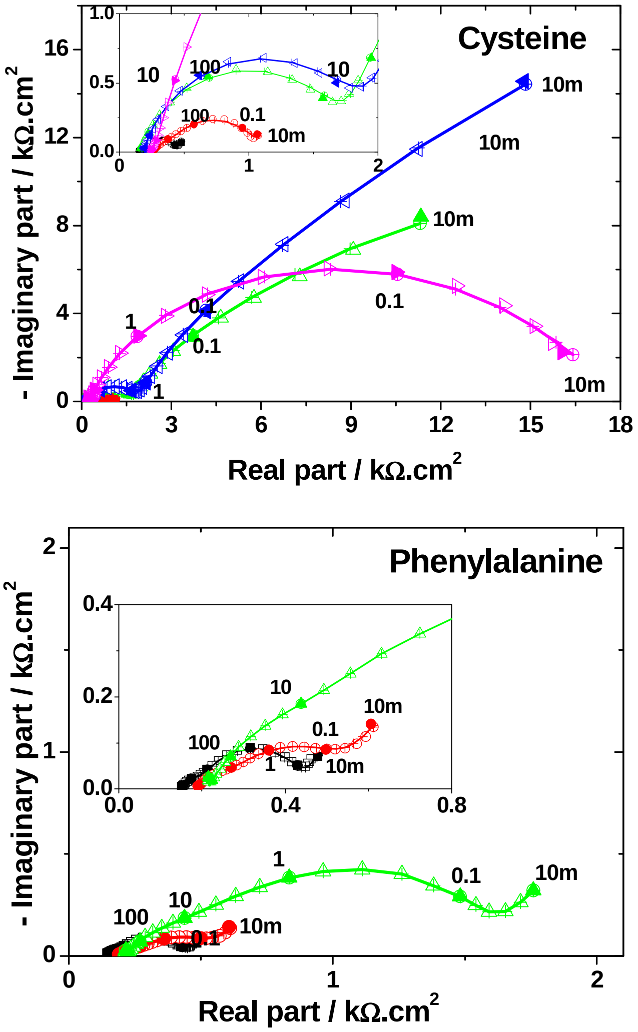


Figure 2. Nyquist plots of bronze electrode in 0.2 g/L Na_2SO_4 + 0.2 g/L $NaHCO_3$ (pH3) solution, in the absence and in the presence of different concentrations of amino acids (mM): (■) 0; (●) 0.1; (▲); 1; (▼) 10; (▶) 50.
The symbol (—+—) corresponds to the fitted data. Frequencies are expressed in Hz.

As can be seen in Fig. 2, the impedance response of bronze in uninhibited solution changed after the addition of the amino acids; the increase of low frequency limit of the impedance (polarisation resistance) in the presence of the organic compounds confirms the inhibitive properties exerted by the amino acids on bronze corrosion in strong acidic solution.

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 Fig. 3 was adopted to carry out a non-linear regression calculation with a Simplex method. This circuit was formerly used in similar systems in order to explain the copper corrosion in chloride solution of different pH values [24] or the bronze corrosion in the presence of thiadiazole derivatives [3].

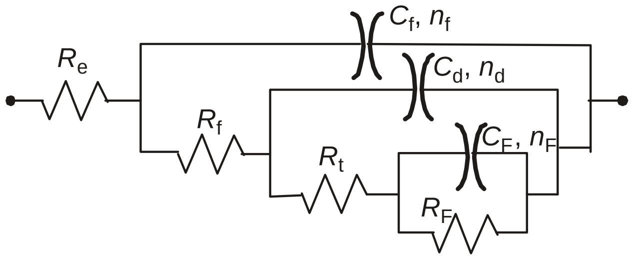


Figure 3. (3RC) equivalent electrical circuit used for computer fitting of the experimental data

The origin of the variables used in the (3RC) equivalent circuit from Fig. 3 were ascribed as follows [3, 25]: R_e-electrolyte resistance; R_f - resistance representing the ionic leakage through pores of a dielectric thin film formed on the surface that is reinforced in the presence of the inhibitors and by the ionic conduction through its pore; C_f - capacitance due to the dielectric nature of the surface film (corrosion products); R_t - charge transfer resistance; C_d - double layer capacitance at the bronze|electrolyte interface; R_F - faradic resistance of the corrosion products layer accumulated at the interface; C_F - faradic capacitance due to a redox process taking place at the electrode surface, probable involving the corrosion products; 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:

$$Z = \frac{R}{1+(j\cdot\omega\cdot R\cdot C)^n} \qquad (1)$$

where: $0 < n \leq 1$

The results of non-liner regression calculation with Simplex method (cross symbols) are superimposed to the experimental data in Fig. 2 and the obtained impedance parameters are given in Table 2.

The fine overlap between the experimental and the calculated data (cross symbols) observed in Fig. 2 proves that the chosen equivalent electrical circuits properly reproduce the experimental data obtained in the absence and in the presence of different concentrations of amino acids, respectively.

TABLE 2. Parameter values for bronze corrosion calculated by non-linear regression of the impedance data using the equivalent electrical circuits from Fig. 3.

Inhibitor conc. (mM)	R_e (Ω cm^2)	R_f (Ω cm^2)	C_f (μF/cm^2)	R_t (Ω cm^2)	C_d (μF/cm^2)	R_F (Ω cm^2)	C_F (mF/cm^2)	R_p^* (Ω cm^2)	IE (%)
0	149.17	86.06	49.72	220.64	520.59	1329.23	276.80	1635.93	-
Cys 0.1	256.76	289.54	69.71	560.39	389.26	3684.40	192.72	4534.33	6.39
1	158.85	1654.30	1.74	6549.50	343.38	15136	1.37	23339.80	92.99
10	185.29	1790.30	1.42	17013	219.12	34090	0.071	52893.30	96.91
50	238.21	138	9.94	11157	16.30	5648	3.58	16943	90.34
PhAla 1	187.20	134.25	59.54	255.91	103.23	1718.3	559.50	2108.46	22.41
10	175.29	198.58	54.67	535.68	346.25	2689.91	80.46	3424.17	52.22

$^*R_p=R_f+R_t+R_F$

As expected, the film resistance R_f increases and attains the maximum values in the presence of both amino acids at a concentration of 10 mM. In the same time, the values of C_f decrease proving that the surface film formed in presence of these optimum concentrations of organic compounds is probably thicker and less permeable.

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 [26].

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 [27-28].

In order to evaluate the anticorrosive effectiveness of the amino acids, their inhibition efficiency (*IE*) was calculated using the polarization resistance values, according to the following equation:

$$IE(\%) = 100 \cdot \frac{i^0_{corr} - i_{corr}}{i_{corr}} \qquad (2)$$

where R_p and R^0_p are the polarisation resistances in electrolytes with and without amino acids, respectively.

From Table 2 it is clearly 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. The exception appears in the case of Cys where a decrease of the R_p value was observed at a further increase of its concentration from 10 mM to 50 mM. This phenomenon is consistent with the results obtained for other inhibitors [29] and could be a consequence of deterioration of the adsorbed inhibitor layer on bronze surface.

In strong acidic solution, the maximum inhibition efficiency values were obtained in the presence of the optimum concentration of amino acids: 10 mM Cys and 10 mM PhAla.

The effectiveness of the corrosion organic inhibitors is related to the extent to which they absorb and cover the metallic surface. The adsorption process mainly depends on the number of adsorption sites in the inhibitors molecule and their charge density, molecular size and interaction mode with the metallic surface [17].

In acidic solutions, the amino acid molecules occurs in its protonated form and could be adsorbed on the electrodic surface through the nitrogen, the oxygen or sulphur atoms, which form a blocking barrier to metallic surface and decrease the corrosion rate.

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 [12, 30]. In the case of phenylalanine, the phenyl- ring could exert a steric hindrance, which affects the adsorption of the organic molecule on bronze surface.

3.3. SEM analysis

Fig. 4a 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 the bronze surface is covered with a layer of corrosion products.

The slight inhibiting effect exerted by PhAla reduced the roughness of the bronze surface, as can be seen in Fig. 4b. In contrast, in the presence of the optimum concentration of Cys (10 mM) almost no corrosion is visible on the metallic surface (Fig 4c), confirming the marked inhibiting efficiency of Cys at this concentration, which is in agreement with the electrochemical results.

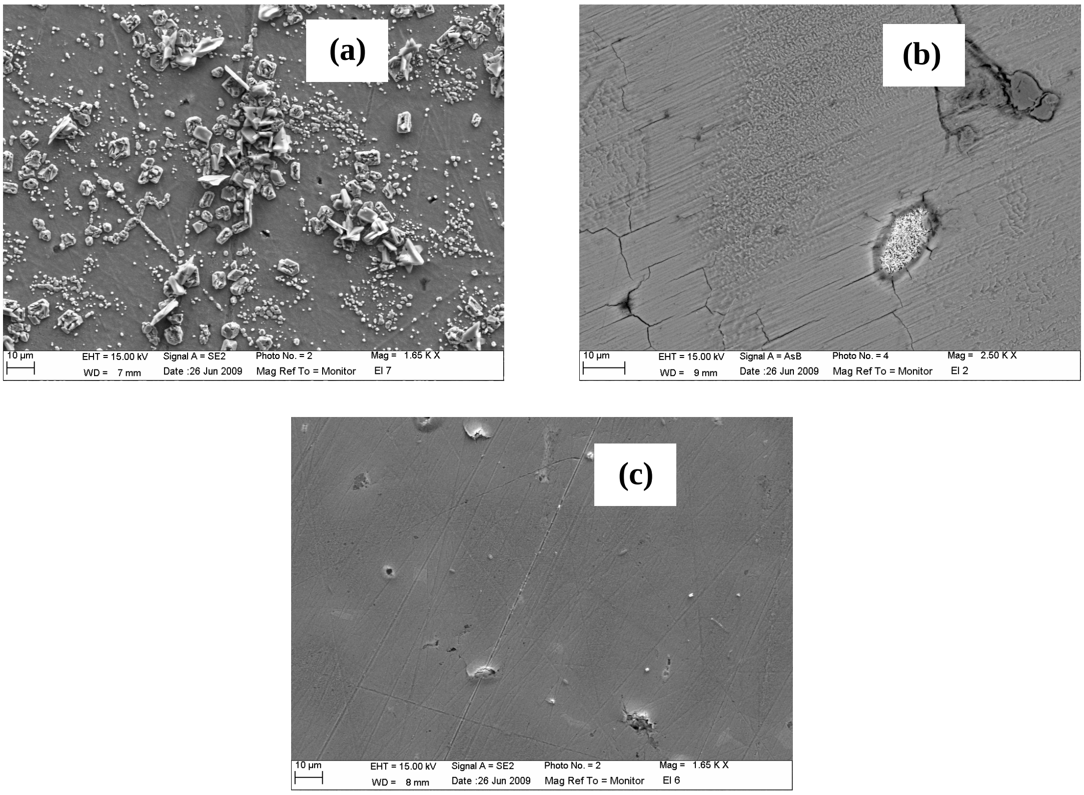


Figure 4. SEM micrograph of the bronze surface obtained after 66 hours immersion in 0.2 g/L $NaHCO_3$ + 0.2 g/L Na_2SO_4 (pH 3) in the absence (a) and in the presence of: (b) 1 mM PhAla and (c) 10 mM Cys

4. Conclusions

Our study reports the effects of two innoxious amino acids (cysteine and phenylalanine) on bronze corrosion in a strong acidic solution of 0.2 g/L Na_2SO_4 + 0.2 g/L $NaHCO_3$ at pH 3 by open-circuit potential measurements, electrochemical impedance spectroscopy and SEM investigations.

The electrochemical measurements demonstrate the inhibitive properties exerted by the investigated amino acids on bronze corrosion in strong acidic solution. Disregarding their molecular structure, each amino acid exerts a more pronounced inhibiting effect on the oxygen cathodic reduction than on the copper dissolution process, as attested by the significant shift of the corrosion potential towards negative values.

In the investigated experimental conditions, the optimum concentrations of amino acids were: 10 mM Cys (96.91 %) and 10 mM PhAla (52.22 %).

Cysteine was proved to be a very promising environmentally-safe alternative to the harmful corrosion inhibitors used for the protection of bronze against corrosion in aggressive media.

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