STUDIA UNIVERSITATIS BABEŞ-BOLYAI, CHEMIA, LIV, 3, 2009

CORROSION INHIBITION OF BRONZE BY AMINO ACIDS IN AQUEOUS ACIDIC SOLUTIONS

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ABSTRACT. The electrochemical behavior of bronze in an aerated solution of 0.2 g/L Na_2SO_4 + 0.2 g/L $NaHCO_3$ (pH=5), in the absence and in the presence of different amino acids was studied using open-circuit potential and electrochemical impedance spectroscopy measurements. The investigated amino acids were: glutamic acid (Glu), arginine (Arg), histidine (His), methionine (Met) and cysteine (Cys).

The impedance measurements revealed that the bronze interface in the presence of the amino acids could be suitably represented by a 3RC equivalent electrical circuit. The magnitude of polarization resistance, determined from the impedance spectra, and the efficiency of corrosion inhibition were found to significantly depend on the structure of amino acids. The protection efficiencies of the investigated compounds decrease in the order: Cys > Glu > Met > Arg > His.

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

INTRODUCTION

One of the most efficient methods for protecting metals from degradation is the use of corrosion inhibitors. Various types of organic compounds, especially nitrogen, sulphur and oxygen containing substances have been widely used as corrosion inhibitors in various aggressive media [1-11]. The effectiveness of heterocyclic molecules as corrosion inhibitors is based on their ability to adsorb on the metallic surface and to form an organic layer which protects the metal from corrosion [5-12]. The adsorption of inhibitors takes place through the heteroatoms (nitrogen, oxygen and sulfur), aromatic rings or triple bounds. Generally, the inhibition efficiency increases in the following order: O < N < S [12].

In spite of their effectiveness, most of the heterocyclic compounds used as corrosion inhibitors are highly toxic and their replacement by "green" inhibitors is desirable [13-14].

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Among the organic compounds tested as environmental friendly corrosion inhibitors, amino acids have been reported as promising alternatives to the toxic inhibitors. They are innoxious, biodegradable, soluble in aqueous media, relatively cheap and easy to produce at high purity [12]. These properties would justify the use of amino acids as corrosion inhibitors.

In the last years, various works focused on the investigation of the anticorrosive properties of different amino acids on aluminium [15], steel [16-19], vanadium [20], lead [21], and alloys [12] corrosion in various aggressive media.

Inhibition of copper corrosion by amino acids has also aroused interests. The investigations revealed that cysteine (Cys) 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.

K. Ismail [13] reported that Cys acts 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. The presence of Cu^{2+} ions increases the inhibition efficiency of Cys up to 90%. The adsorption of Cys on the copper surface in neutral and acidic chloride solutions obeys the Langmuir adsorption isotherm. Matos *et al.* [22] found that Cys inhibits the anodic dissolution of copper in sulphuric acid media at low polarisation due to formation of the cysteine–Cu (I) intermediate. At high overpotentials, Cys has no influence on anodic process.

Zang *et al.* [23] studied the inhibiting effect of serine (Ser), threonine (Thr) and glutamic acid (Glu) on copper corrosion in an aerated 0.5 M HCl solution. They reported that the amino acids act as cathodic inhibitors due to their adsorption on the metallic surface through both nitrogen and oxygen atoms, which forms a blocking barrier to copper dissolution. The inhibition action of the above-mentioned amino acids decrease in the order: Glu > Thr > Ser.

A limited inhibiting effect on copper corrosion in 0.5 M HCl was also noticed in the presence of aspartic acid (Asp), asparagine (Asn), glutamine (Gln) and glutamic acid (Glu) [24]. The efficiency of these inhibitors depends on their chemical structure and decreases in the following order: Gln > Asn > Glu > Asp. The results obtained from the potentiodynamic polarisation indicate that the four amino acids are mixed-type inhibitors and their protection efficiency increases with increasing their concentration up to 0.1 M.

Zang *et al.* [25] also showed that alanine (Ala) and cysteine (Cys) at a concentration of 10^{-5} M act as anodic inhibitors against copper corrosion in 0.5 M HCl. The maximum protection efficiency was obtained in the presence of Cys (58.7%). The inhibition efficiencies of Ala and Cys were found to be higher than the one of the benzotriazole (BTA), which is widely known as the most efficient corrosion inhibitor of copper and its alloys.

Methionine (Met) has shown limited inhibiting properties for copper corrosion in 0.5 M HCl. The presence of Zn^{2+} ions in the corrosive solution increases the inhibition efficiency up to 92% [26].

Barouni *et al.* [27] measured the effect of valine (Val), glycine (Gly), lysine (Lys), arginine (Arg) and Cys on the copper corrosion in aerated nitric acid solution. They reported that some amino acids (Arg, Cys, Lys) were able to decrease the dissolution rate, while others, such as, Val and Gly actually seems to accelerate the corrosion phenomenon. The inhibition efficiencies determined from polarisation measurements vary in the order: Val (-15%) < Gly (-4%) < Arg (38%) < Lys (54%) < Cys (61%).

Furthermore, in a recent paper we have reported the beneficial effect exerted by Cys and Ala on bronze corrosion in an aerated electrolyte containing Na_2SO_4 and $NaHCO_3$ at pH=5. The electrochemical investigations showed that the two innoxious amino acids have fairly good inhibiting properties for bronze corrosion, the best anticorrosive protection being obtained in the presence of 0.1 mM Cys (90%) [28].

In the present study, four environmentally safe amino acids were tested as inhibitors on bronze corrosion in an aerated solution of 0.2 g/L Na_2SO_4 + 0.2 g/L NaHCO3 (pH=5). The compounds examined were: glutamic acid (Glu), methionine (Met), histidine (His) and arginine (Arg). Some of our previous results obtained using cysteine (Cys) as bronze corrosion inhibitors will also be mentioned for comparison sake.

In order to establish some correlation between the molecular structure of the amino acids and their inhibiting efficiency, as well as the optimum concentration of each amino acid as bronze corrosion inhibitor, conventional electrochemical techniques, such as open-circuit potential (ocp) and electrochemical impedance spectroscopy (EIS) measurements were used.

RESULTS AND DISCUSSION

Open-circuit potential measurements

The evolution of the open-circuit potential (ocp) for bronze over 60 minutes immersion in the corrosive solution in the absence and presence of different concentration of amino acids is illustrated in Figure 1.

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

Generally, the steady state potential (E_{ss}) was reached within less than 30 minutes after the electrode immersion in the corrosive media.

The value of the steady-state potential of bronze in blank solution was + 48.70 mV *vs.* SCE.

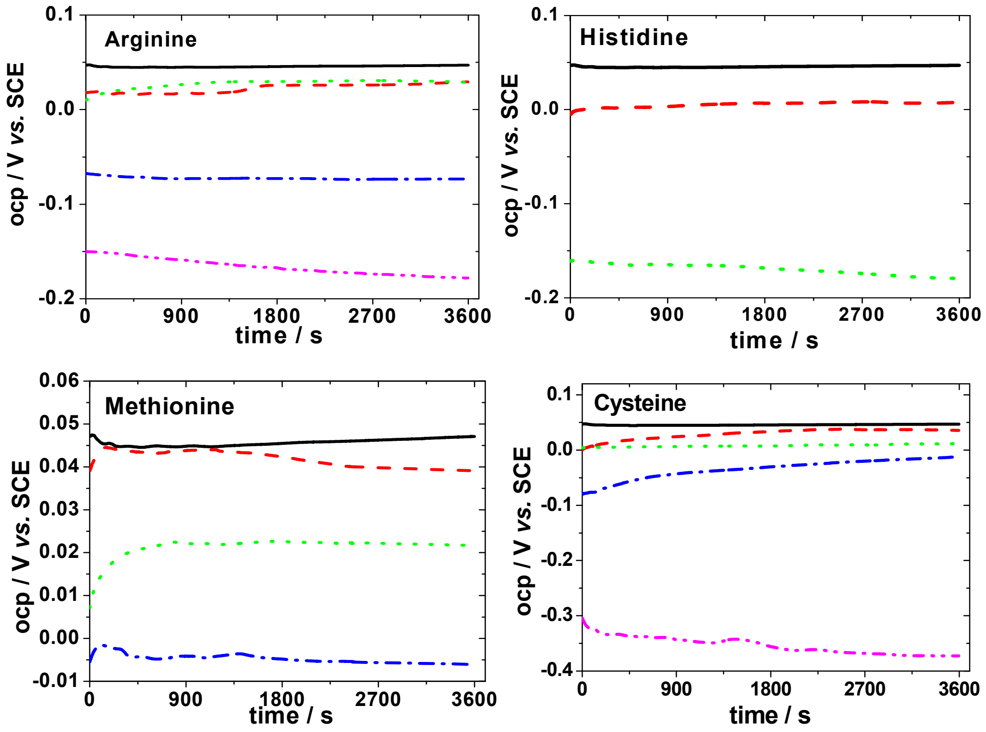


Figure 1. Variation of the open-circuit potential in time for bronze electrode after immersion in the corrosive media in the absence and in the presence of amino acids at different concentrations of amino acids (mM): (—) 0; (— —) 0.01; (·····); 0.1; (—·—) 1; (—··—) 10.

The values of E_{ss} obtained in the presence of different concentrations of amino acids are presented in Table 1.

Table 1. The values of the steady-state potential of bronze in electrolytes containing different concentrations of amino acids

Amino acids conc. (mM)	**E_{ss} / mV *vs.* SCE**				
	Glu	**His**	**Arg**	**Met**	**Cys**
0.01	+47.11	-	+32.71	+40.10	+35.93
0.1	+45.48	+19.78	+28.54	+22.17	-11.77
1	+26.72	+ 7.56	-73.43	- 5.33	-13.33
10	-	-17.95	-177.51	-	-327.60

The value of the shift in the E_{ss} is related to the structure of the amino acid and its concentration in the electrolyte. Thus, for Cys and Arg the maximum negative shifts occur at concentrations of 1 mM and 10 mM, respectively.

Addition of Glu, Met and His at concentrations of 1 mM has a less pronounced effect on the E_{ss} value.

Generally, the potential shift can be attributed to the adsorption of the amino acids molecules on the active sites and/or the deposition of corrosion products on the electrode surface [steel, Pb, carbon steel].

A precise categorization of a compound as an anodic or cathodic inhibitor requires an E_{ss} displacement of up to 85 mV with respect to the blank corrosive solution [16]. The magnitude of the E_{ss} displacements suggests that at low concentrations (0.01-0.1 mM) the amino acids simultaneously affect the cathodic and anodic reactions, while at higher concentrations (1 and 10 mM) they predominantly influence the cathodic reduction, probably acting as barriers to the diffusion of oxygen molecules from the solution to the bronze surface.

Electrochemical impedance spectroscopy measurements

In order to provide insight into the characteristics and kinetics of bronze corrosion in the presence of amino acids, the electrochemical process occurring at the open-circuit potential was examined by electrochemical impedance spectroscopy.

As it is well-know [29], the most important advance of the electrochemical impedance spectroscopy is the fact that it enables the fitting of the experimental impedance data to theoretical values according to equivalent circuit models allowing the understanding of the corrosion inhibition mechanism and the suggestion of the suitable electrical model that explains the behaviour of the metal under different conditions.

Nyquist plots collected after 60 minutes immersion of the bronze in solutions without and with various concentrations of amino acids are presented in Figure 2.

The impedance spectra obtained in the absence and in the presence of amino acids display a capacitive behaviour in the whole frequency domain and the low frequency limit of the impedance significantly increases by addition of various concentrations of organic compounds in the corrosive solution.

In order to calculate the numerical values of the parameters that describe the electrochemical system and to verify the mechanistic model of bronze corrosion in the presence of the amino acids, the impedance spectra were appropriately analyzed by fitting the experimental data to the electrical equivalent circuits presented in Figure 3.

We have recently reported and discussed [5, 28] that the impedance spectra obtained for bronze corrosion in the absence of any inhibitor could be suitable described by two R-C ladder circuits, while in the presence of some inhibitors (*i.e.* Cys and Ala), three capacitive loops, though badly separated each other, were necessary for computer fitting of experimental data with an electrical equivalent circuit.

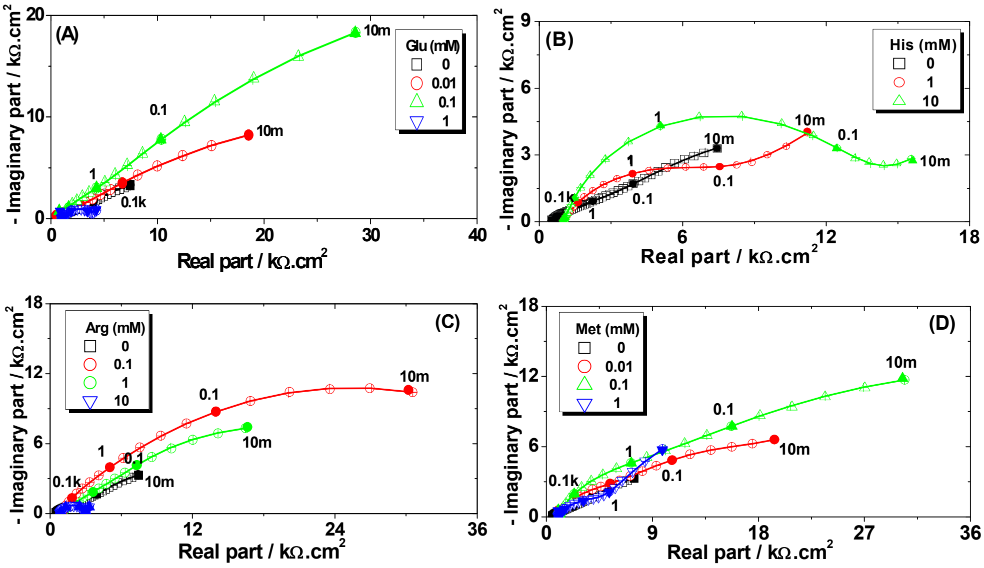


Figure 2. Nyquist plots of bronze electrode in 0.2 g/L Na_2SO_4 + 0.2 g/L $NaHCO_3$ (pH=5) solution, in the absence and in the presence of different amino acids: (A) glutamic acid; (B) histidine; (C) arginine; (D) methionine. The symbol (—+—) corresponds to the simulated spectra. Frequencies are expressed in Hz.

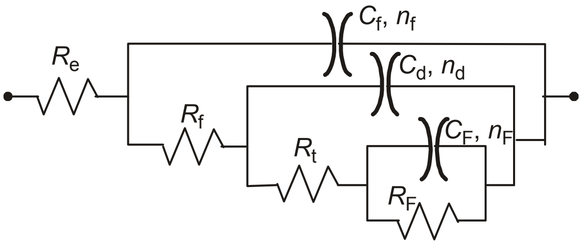


Figure 3. Equivalent electrical circuit used for computer fitting of experimental data

In the present work, the (3RC) electrical circuit was also adopted for carrying out a non-linear regression calculation of the impedance data obtained in the presence of the amino acids (Glu, His, Arg, Met) using a Simplex method.

The origin of the various variables used in the equivalent circuit from Figure 3 were ascribed as follows [5, 28]: 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 was calculated according to the following equation:

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

C has the dimension of F cm^{-2}, and corresponds to the value at the frequency of the apex in Nyquist diagram ($\omega RC = 1$) [5].

Table 2 summarises the results of the regression calculations with the electrical circuits from Figure 3. For comparison, the values of the impedance parameters previously obtained in the absence and in the presence of the optimum concentration of Cys (0.1 mM) [28] were included in the Table 2, as well.

The fine overlap between the experimental and the calculated data (cross symbols) observed in Figure 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.

In presence of oxidation–reduction process at the electrode surface, the polarization resistance R_p is the parameter the most closely related to the corrosion rate [5].

The values of the polarisation resistance, R_p were determined as the sum ($R_f + R_t + R_F$) from the resistances values determined by regression calculation (Table 2).

In most cases, the addition of the amino acids in the corrosive solution decreases the bronze corrosion rate, as attested by the increase of the polarization resistance values. This indicates that amino acids inhibit the bronze corrosion process, probably due to their ability to adsorb and to form a protective layer on the metallic surface. The highest values of the R_p were obtained in the presence of: 0.1 mM Glu; 0.1 mM Arg; 10 mM His and 0.1 mM Met.

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:

$$\mathrm{IE}(\%) = 100 \cdot \frac{\mathrm{R_p^0} - \mathrm{R_p}}{\mathrm{R_p}} \tag{2}$$

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

Table 2. The results of non-linear regression of the impedance spectra presented in Figure 2

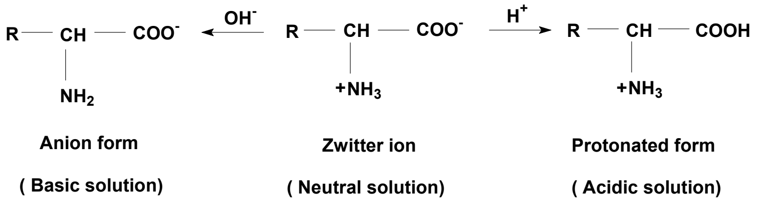
Amino acids conc. (mM)	**R_e (kΩcm^2)**	**R_f (kΩcm^2)**	**C_f (μF/cm^2)**	**R_t (kΩcm^2)**	**C_d (μF/cm^2)**	**R_F (kΩcm^2)**	**C_F (mF/cm^2)**	**R_p (kΩcm^2)**	**IE (%)**
0	0.46	-	-	3.34	36.84	12.66	1.65	16.01	-
Glu 0.01	1.04	0.56	0.13	4.14	62.68	38.22	0.36	42.92	62.70
0.1	9.84.	3.94	0.14	15.28	85.99	79.23	0.038	98.45	**83.74**
1	9.77	0.55	0.18	2.68	108.74	1.63	19.32	4.86	-
His 1	0.99	0.16	5.33	10.62	15.06	9.80	5.45	20.58	2.19
10	1.01	0.34	5.53	17.74	3.05	10.04	3.82	28.12	**43.06**
Arg 0.01	0.89	2.65	3.28	4.17	13.35	10.49	1.82	17.31	7.51
0.1	0.97	5.31	10.73	9.42	61.20	30.10	3.20	44.83	**64.28**
1	0.79	0.085	4.21	5.20	19.69	24.00	1.30	29.29	45.34
10	0.82	0.051	2.09	2.21	7.54	3.64	35.75	5.90	-
Met 0.01	1.01	5.71	9.69	20.90	29.87	15.00	6.14	41.61	61.52
0.1	1.02	3.96	3.83	33.82	1.67	53.89	0.2	91.67	**82.54**
1	0.99	3.47	27.50	5.63	57.85	13.68	0.49	22.78	29.73
Cys 0.1	1.08	1.53	0.94	42.55	1.95	126.71	0.031	170.79	**90.63**

$^*R_p=R_f + R_t + R_F$

As it can be seen from the last column of table 2, the anticorrosive protection offered by the investigated amino acids on bronze is relatively weak at low concentrations. As the amino acid concentration increases, their inhibition efficiencies increase and reach a maximum value in the presence of optimum concentration of the inhibitors. Nevertheless, a further increases of the amino acids concentration leads to a decrease of their protective effectiveness. This phenomenon could be probably attributed to the saturation of the bronze surface with inhibitor molecules at a certain concentration [13].

As previously mentioned [30], 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 [24].

In general, the amino acid molecule occurs in its protonated form in acidic solution according to the following equilibrium [13, 20]:



In acidic solutions, the amino acid molecules 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 [20].

In the investigated experimental conditions, the inhibition efficiency of the amino acids as bronze corrosion inhibitors decreases in the order: Cys > Glu > Met > Arg > His.

As expected, among the studied amino acids, Cys exhibits the best inhibition efficiency compared with the five others, probably because its adsorption on bronze as bidentate ligand in which surface coordination is taking place through both the amino group and the –S– moiety [5, 13, 17].

The relatively good anticorrosive protection of Glu on bronze corrosion could be explained if we take into consideration that the molecule has a smaller net positive charge of N atom and a more net negative charge of O atoms [23], which can contribute to its adsorption on the bronze surface. Consequently, the improved inhibition of glutamic acid could be due to the stabilization of its adsorption on the metallic surface by the oxygen atoms in its structure.

In the case of metionine, the electron-donor group ($-CH_3$) attached to the S atom could exert a steric hindrance [17] which probably affects the adsorption of the organic molecule on bronze surface. Therefore, the inhibition efficiency of Met slightly decreases as compared to Glu.

Although Arg has a radical which contains 3 nitrogen atoms, its effectiveness is lower probably due to the existence of a tautomeric and steric hindrance at the N atoms [15]. The lower inhibition efficiency of His compared to Arg could be due to the fact that His contains a cyclic imidazole group which probably give a smaller surface coverage than the straight chain structure of the radical in Arg. Moreover, the adsorption of His on the metallic surface is probably taking place through only one -N atom in the secondary amine group [15].

CONCLUSIONS

Our study reports the effects of several amino acids (glutamic acid, arginine, histidine, methionine and cysteine) on bronze corrosion in an aerated solution of 0.2 g/L Na_2SO_4 + 0.2 g/L $NaHCO_3$ at pH 5 using open-circuit potential measurements and electrochemical impedance spectroscopy.

The electrochemical measurements showed that all investigated amino acids present inhibition properties on bronze corrosion.

The molecular structure of amino acids significantly influences the magnitude of R_p values and, consequently, their inhibition efficiency.

The order of anticorrosive effectiveness of the inhibitors was Cys > Glu > Met > Arg > His. The variation of the inhibition efficiency with the structure of the amino acids was interpreted taking into consideration the number of adsorption active centres in the molecule, the adsorption mode and the molecular size of the compounds.

In the investigated experimental conditions, the optimum concentration of each amino acids was relatively low (0.1 mM), except for the case of His, when a concentration of 10 mM was necessary to attain its maximum inhibition efficiency.

EXPERIMENTAL SECTION

Reagents

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 by addition of dilute H_2SO_4. This electrolyte corresponds to an acidic rain in an urban environment. The solutions used in this study were prepared using analytical grade reagents (Merk, Darmstadt, Germany) and ion-exchanged water.

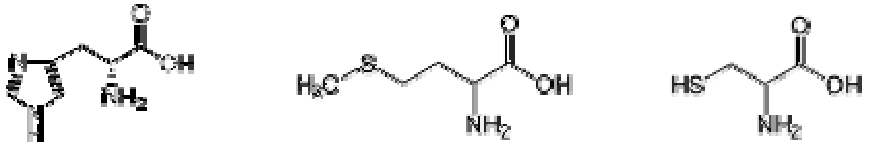
The amino acids were dissolved in the electrolyte solution to the concentration of 0.01-10 mM. They were purchased from Sigma-Aldrich and used as received.

The amino acids used in the electrochemical investigations are:

1. Acidic amino acids: glutamic acid.
2. Basic amino acids: histidine and arginine.
3. Sulphur-containing amino acids: methionine and cysteine.

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

glutamic acid (**Glu**) arginine (**Arg**)



histidine (**His**) methionine (**Met**) cysteine (**Cys**)

Scheme 1. Molecular structure of the investigated amino acids

Electrochemical measurements

The investigation of the inhibiting properties of the amino acids on bronze corrosion was performed by open-circuit potential measurements and electrochemical impedance spectroscopy.

An electrochemical cell with a three-electrode configuration was used; a large platinum grid and a saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively. To avoid the electrolyte infiltration, the working electrode was made of a bronze cylinder rod which was first covered with cataphoretic paint layer (PGG; W742 and P962), and cured at 150°C for 15 minutes. Then, the bronze cylinder was embedded into an epoxy resin leaving only a circular cross section (0.38 cm^2) in contact with the corrosive solution. The composition of the working electrode is presented in Table 3.

Table 3. Weight composition (%) of the bronze working electrode

Cu	Sn	Pb	Zn	Sb	Ni	Fe	Mn	As	S	P, Si
87.975	6.014	4.02	1.172	0.299	0.181	0.11	0.002	0.033	0.19	0.004

Prior to use, the bronze surface was mechanically polished using grit paper of 600 and 1200 and then rinsed thoroughly with distilled water.

Electrochemical experiments were performed using a PAR model 2273 potentiostat controlled by a PC computer.

Electrochemical impedance measurements were carried out at the open circuit potential after 60 minutes 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.

ACKNOWLEDGMENTS

The financial support from CNCSIS under the project PNCDI II-Idei, contract no. 569/2009, CNCSIS code 17 is gratefully acknowledged.

REFERENCES

1. H. Otmacic, E. Stupnisek-Lisac, *Electrochimica Acta*, **2003**, *48,* 985.
2. K. Es-Salah, M. Keddam, K. Rahmouni, A. Srhiri, H. Takenouti, *Electrochimica Acta*, **2004**, *49*, 2771.
3. A. Dermaj, N. Hajjaji, S. Joiret, K. Rahmouni, A. Srhiri, H. Takenouti, V. Vivier, *Electrochimica Acta*, **2007**, *52*, 4654.
4. K. Rahmouni, N. Hajjaji, M. Keddam, A. Srhiri, H. Takenouti, *Electrochimica Acta*, **2007**, *52* 7519.

5. L. Muresan, S. Varvara, E. Stupnisek-Lisac, H. Otmacic, K. Marusic, S. Horvat Kurbegovic, L. Robbiola, K. Rahmouni, H. Takenouti, *Electrochimica Acta*, **2007**, *52*, 7770.
6. H. Ma, S. Chen, L. Niu, S. Zhao, S. Li, D. Li, *Journal of Applied Electrochemistry*, **2002**, *32*, 65.
7. J.B. Matos, L.P. Pereira, S.M.L. Agostinho, O.E. Barcia, G.G.O. Cordeiro, E. D' Elia, *Journal of Electroanalytical Chemistry*, **2004**, *570*, 91.
8. S.A. Abd El-Maksoud, *Electrochimica Acta*, **2004**, *49*, 4205.
9. K.F. Khaled, *Materials Chemistry and Physics*, **2008**, *112*, 104.
10. D. Zhang, L. Gao, G. Zhou, K.Y. Lee*, Journal of Applied Electrochemistry*, **2008**, *38*, 71.
11. S.M. Milic, M.M. Antonijevic*, Corrosion Science*, **2009**, *51*, 28.
12. M.A. Kiani, M.F. Mousavi, S. Ghasemi, M. Shamsipur, S.H. Kazemi, *Corrosion Science,* **2008**, *50*, 1035.
13. K. M. Ismail, *Electrochimica Acta*, **2007**, *52*, 7811.
14. E. Stupnisek-Lisac, A. Gazivoda, M. Madzarac, *Electrochimica Acta*, **2002**, *47*, 4189.
15. A.A. E.Shafei, M.N.H. Moussa, A.A. ElFar, *Journal of Applied Electrochemistry*, **1997**, *27* 1075.
16. E. Oguzie, Y. Li, F.H. Wang*, Electrochimica Acta*, **2007**, *53*, 909.
17. M. S. Morad, *Journal of Applied Electrochemistry*, **2008**, *38*, 1509.
18. A.B. Silva, S.M.L. Agostinho, O.E. Barcia, G.G.O. Cordeiro, E.D'Elia, *Corrosion Science*, **2006**, *48*, 3668.
19. P. Singh, K. Bhrara, G. Singh, *Applied Surface Science*, **2008**, *254*, 5927.
20. M.M. El-Rabiee, N.H. Helal, Gh.M. A. El-Hafez, W.A. Badawy, *Journal of Alloys and Compounds*, **2008**, *459*, 466.
21. N.H. Helal, M.M. El-Rabiee, Gh.M. Abd El-Hafez, W.A. Badawy, *Journal of Alloys and Compounds*, **2008**, *456*, 372.
22. J.B. Matos, L.P. Pereira, S.M.L. Agostinho, O.E. Barcia, G.G.O. Cordeiro, E. Delia, *Journal of Electroanalytical Chemistry*, **2004**, *570*, 91.
23. D.-Q. Zhang, Q.-R. Cai, L.-X. Gao, K.Y. Lee, *Corrosion Science*, **2008**, *50*, 3615.
24. D.-Q. Zhang, Q.-R. Cai, X.-M. He, L.-X. Gao, G.-D. Zhou, *Materials Chemistry and Physics*, **2008**, *112*, 353.
25. D.-Q. Zhang, L.-X. Gao, G.-D. Zhou, *Journal of Applied Electrochemistry*, **2005** *35*, 1081.
26. D.-Q. Zhang, Q.-R. Cai, X.-M. He, L.-X. Gao, G.S. Kim, *Materials Chemistry and Physics*, **2009**, *114*, 612.
27. K. Bauroni, L. Bazzi, R. Saghi, M. Mihit, B. Hammouti, A. Albourine, S. E. Issami, *Materials Letters*, **2008**, *62*, 3325.
28. S. Varvara, M. Popa, G. Rustoiu, R. Bostan, L. Muresan, *Studia Universitatis Babes-Bolyai, Chemia,* **2009**, in press.
29. A. J. Bard, L. R. Faulkner, “Electrochemical methods. Fundamentals and Applications” (2nd Edition), John Wiley & Sons Publisher, New York, **2001**, chapter 10.
30. E. Stupnisek-Lisac, A. Gazivoda, M. Madzarac, *Electrochimica Acta*, **2002**, *47*, 4189.